

PRELIMINARY STUDY OF  
SOURCES OF CARBON TETRACHLORIDE

Final Report



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by  
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## EXECUTIVE SUMMARY

This report provides preliminary information on sources of air emissions of carbon tetrachloride. This information is intended to assist EPA in the regulatory decision-making process. Potentially significant sources are identified and described. Source descriptions include general information on each industry and production process, as well as emission estimates, applicable regulations and control technology. Principal sources of carbon tetrachloride air emissions are as follows:

- o Carbon tetrachloride production,
- o Chlorofluorocarbon (CFC) 11 and 12 production,
- o Methanol hydrochlorination/methyl chloride chlorination,
- o Ethylene dichloride production,
- o Perchloroethylene and trichloroethylene production from ethylene dichloride,
- o Grain fumigant formulation and use, and
- o Pharmaceutical manufacturing.

Other sources identified include production processes for phosgene/isocyanate/polyurethane, pesticides, synthetic rubber, and carbon tetrabromide.

In addition to describing each of these source categories, this report also presents preliminary information on carbon tetrachloride emissions and control costs for carbon tetrachloride production plants and plants which produce CFC 11 and 12 from carbon tetrachloride. Uncontrolled emissions were estimated for each type of source at these plants, using available model plant emission factors and production data for individual sources. Controlled emissions and control costs were estimated for two control options: Option 1 represents a baseline

level of control which would be expected without further regulatory activity, consisting of the most stringent control provided by known existing controls, applicable State regulations, or Group III control techniques guidelines (CTG). It was assumed that Group III CTGs will apply in areas which have received ozone NAAQS attainment date extensions beyond 1982, and that States required to adopt such CTGs will do so. Sources were also assumed to be in full compliance with applicable State regulations. Option 2 consists of estimated best control (EBC) for each significant emission source, chosen from the highest control levels known to be in use, as identified under Option 1, and other available high-efficiency controls, such as best demonstrated technology developed for new source performance standards.

The carbon tetrachloride emissions, control data, and costs of control in this report are based on information obtained from existing EPA reports and other published sources, from EPA data files on the synthetic organic chemical manufacturing industry, and from telephone contacts with control equipment vendors, and EPA, State and local agency personnel. This study did not include plant visits, source testing, or other original data gathering. The available references contain very little data on plant-specific emissions of carbon tetrachloride and on related control costs. In the source assessments for carbon tetrachloride and CFC 11/12 production, available data were used to develop emissions and costs for representative model plants. Estimated emissions and control costs for individual plants were then derived from model plant data by assuming that emissions and costs are directly proportional to carbon tetrachloride production. This methodology is described in more detail in Chapter 1, and examples and supporting data are presented in Appendices A and B. Resulting estimates are summarized in Tables 1 and 2. Due to the number of simplifications and assumptions involved in this approach, the emissions and control cost estimates presented in this report must be considered preliminary.

TABLE 1. SUMMARY: EMISSIONS OF CARBON TETRACHLORIDE FROM CARBON TETRACHLORIDE AND CHLOROFLUOROCARBON 11/12 PRODUCTION

Source category	Carbon tetrachloride emissions, Mg/yr		
	Uncontrolled	Option 1	Option 2
<u>Perchloroethylene co-product process</u>			
Process	1.2	1.1	0.1
Fugitive	203	200	89
Storage	185	57	9.3
Loading	52	30	5.2
Secondary	1.7	1.2	0.03
<hr/> Subtotal	<hr/> 443	<hr/> 289	<hr/> 104
<u>Methane chlorination process</u>			
Process	5.7	5.6	2.2
Fugitive	80	65	35
Storage	27	8.0	1.4
Loading	10.9	9.2	1.1
Secondary	0.8	0.8	0.8
<hr/> Subtotal	<hr/> 124	<hr/> 89	<hr/> 40
<u>Carbon disulfide process</u>			
Process	7,240	362	18
Fugitive	37	37	16
Storage	50	50	2
Loading	15	15	1
<hr/> Subtotal	<hr/> 7,342	<hr/> 464	<hr/> 37
<u>Chlorofluorocarbon 11/12 process</u>			
Process	11.1	11.1	11.1
Fugitive	40	34	18
Storage	40	7	2
<hr/> Subtotal	<hr/> 91	<hr/> 52	<hr/> 31
<hr/> TOTAL	<hr/> 8,000	<hr/> 894	<hr/> 212

TABLE 2. SUMMARY: COSTS OF CONTROL OF CARBON TETRACHLORIDE EMISSIONS  
FROM CARBON TETRACHLORIDE AND CHLOROFLUOROCARBON 11/12  
PRODUCTION (July 1982 dollars)

Source category	Capital costs		Annualized costs	
	Option 1	Option 2	Option 1	Option 2
<u>Perchloroethylene co-product process</u>				
Process	6,700	40,200	2,100	12,700
Fugitive	8,800 <sup>a</sup>	327,600 <sup>a</sup>	5,000 <sup>a</sup>	152,600 <sup>a</sup>
Storage	2,187,000 <sup>a</sup>	3,833,400 <sup>a</sup>	573,500 <sup>a</sup>	1,028,600 <sup>a</sup>
Loading	468,600	1,085,100	129,000	314,800
Subtotal	2,671,100	5,286,300	709,600	1,508,700
<u>Methane chlorination process</u>				
Process	26,000	549,600	10,900	163,200
Fugitive	63,400	258,400	44,700	150,300
Storage	99,800 <sup>a</sup>	156,800 <sup>a</sup>	27,800 <sup>a</sup>	43,700 <sup>a</sup>
Loading	38,100	251,200	10,300	73,200
Subtotal	227,300	1,216,000	93,700	430,400
<u>Carbon disulfide process</u>				
Process	71,500	242,500	(2,804,000)	(2,856,000)
Fugitive	--	30,700	--	10,000
Storage	--	570,000	--	144,900
Loading	--	83,900	--	19,900
Subtotal	71,500	927,100	(2,804,000)	(2,681,200)
<u>Chlorofluorocarbon 11/12 process</u>				
Fugitive	14,700	46,300	8,500	26,500
Storage	1,837,300	2,966,000	518,700	843,000
Subtotal	1,852,000	3,012,300	527,200	869,500
TOTAL	4,821,900	10,441,700	(1,473,500)	127,400

<sup>a</sup>Storage costs for two-process plants are in totals for perchloroethylene co-product process.

( ) indicates credit

-- indicates no control

There are currently nine carbon tetrachloride production facilities in the U.S., with a total production capacity of 478,000 Mg/yr. Sixty-five percent of this capacity is in Texas and Louisiana, where there are two plants in each State. Other plants are located in West Virginia, Alabama, Kentucky, Kansas, and California. The three carbon tetrachloride production processes and their approximate percentages of national production capacity are as follows: (1) chlorinolysis or chlorination of hydrocarbons with perchloroethylene co-product (70 percent); (2) carbon disulfide chlorination (20 percent); and (3) methane chlorination (10 percent). Three plants use a perchloroethylene co-product process exclusively, while three more use it in conjunction with a methane chlorination process. Two small plants use methane chlorination exclusively. Only one plant currently uses carbon disulfide chlorination, although two other large carbon disulfide-based plants have been closed since 1975.

Six of the nine carbon tetrachloride plants have some control of storage emissions under Option 1. Option 1 also includes loading controls at three plants, process controls at three plants, process fugitive controls at two plants, and secondary emission controls at two plants. Option 1 results in overall reductions over estimated uncontrolled emissions of about 35 percent and 30 percent for the perchloroethylene co-product and methane chlorination processes, respectively. Most of this reduction is due to the storage controls.

Under Option 2, the following were selected as EBC for emission sources common to all three carbon tetrachloride production processes (control efficiencies in parentheses): process fugitive emission control by monthly inspection and repair, with equipment specifications (56 percent); storage emission control by refrigerated condenser (95 percent); and loading control by vapor recovery and refrigerated condenser (90 percent). EBC process controls include a refrigerated condenser for perchloroethylene co-product processes (90 percent), a chloroform-based absorber system controlling two of three methane chlorination process emission points (62 percent), and an additional refrigerated condenser on the existing condenser for the carbon disulfide process (combined control of 99.8 percent).

EBC for secondary emissions at perchloroethylene co-product plants includes steam-stripping of waste caustic, as well as vapor balance, condensation and recycle for waste products (98 percent). Control of the small secondary emissions at methane chlorination plants is not practical, since at least six emission points are involved.

As shown in Table 1, EBC for the three production processes is estimated to result in a total carbon tetrachloride emission reduction of 661 Mg/yr over Option 1, for an incremental control efficiency of about 79 percent. Slightly more than half of this reduction is due to EBC on the process vent at the single carbon disulfide plant, where the plant-wide control efficiency over Option 1 is about 92 percent. Corresponding overall incremental reductions are 185 Mg/yr (64 percent) for the perchloroethylene co-product processes and 49 Mg/yr (55 percent) for the methane chlorination processes.

Table 2 presents preliminary estimates of the total costs of Option 1 and 2 controls for each emission category at carbon tetrachloride plants. For the three plants which use both the perchloroethylene co-product process and methane chlorination, joint product storage was assumed, and all control costs are included in totals for the perchloroethylene co-product process. Costs for Option 2 are totals for implementation of EBC, and are not adjusted to reflect current or anticipated costs under Option 1. Thus these costs represent worst case estimates. Total capital costs for Option 1 and 2 controls for the perchloroethylene co-product process and methane chlorination are estimated at \$2,898,000 and \$6,502,000, and corresponding net annualized costs total \$803,000 and \$1,939,000 for Options 1 and 2, respectively. For the carbon disulfide plant, capital costs are estimated at \$71,500 for Option 1 and \$927,100 for Option 2. Both process controls at this plant result in net credits due to recovery of carbon tetrachloride. Product recovery by the Option 1 control at this plant results in large annual credits for Options 1 and 2 (\$2,804,000 and \$2,681,200).

About 90 percent of domestic carbon tetrachloride use is as a feedstock for production of CFC 11 and 12. There are eight CFC 11/12 production locations, which were estimated to produce 74,000 Mg of CFC 11 and 147,000 Mg of CFC 12 in 1981. Two of these plants are in California, with one each in New Jersey, Kentucky, Illinois, Michigan, Louisiana and Kansas. Plant-specific data on CFC 11/12 production and carbon tetrachloride use are available for only one plant; thus most of the emission and control cost estimates cited in this report are based on CFC 11/12 production capacities which were estimated by assuming uniform distribution of available total CFC capacities at the plant or company level. A total of six plants have Option 1 controls on carbon tetrachloride feedstock storage, and one plant has no storage on site. Option 1 includes process fugitive controls at three plants. There are no Option 1 controls in place or required for carbon tetrachloride process emissions at CFC 11/12 plants. Option 1 is estimated to result in 40 percent control over total uncontrolled emissions of carbon tetrachloride from CFC 11/12 plants. Under Option 2, EBC consists of 56 percent control of process fugitive emissions by a monthly inspection and repair program, with equipment specifications, and 95 percent control of carbon tetrachloride feedstock storage by a refrigerated condenser. There is no EBC for process emissions. As shown in Table 1, applying EBC to all plants is estimated to result in an overall emission reduction over Option 1 of 21 Mg, or 40 percent. Table 2 shows the corresponding estimated capital and net annual costs, which total about \$1,852,000 and \$527,000 respectively for Option 1, and \$3,012,000 and \$870,000 for Option 2.

Three other synthetic organic chemical production processes have been reported to result in incidental formation and emission of small amounts of carbon tetrachloride. These processes include: production of methyl chloride, methylene chloride and chloroform by methanol hydrochlorination and subsequent chlorination of methyl chloride; production of ethylene dichloride; and production of trichloroethylene and perchloroethylene from ethylene dichloride.

There are seven plants in the U.S. producing chlorinated methanes by hydrochlorination of methanol and chlorination of methyl chloride. There are two plants each in West Virginia and Louisiana, and one each in Kentucky, Texas, and Kansas. Carbon tetrachloride is formed in the methyl chloride chlorination step, and can be emitted as process fugitives, as well as from storage and handling of the distillation bottoms. Information is not available on existing controls for these sources, and also is not sufficient to assess applicability of other Option 1 controls or EBC.

There are 19 plants in the U.S. producing ethylene dichloride, and 1 under construction, including 11 plants in Louisiana, 8 plants in Texas and 1 in Kentucky. Ethylene dichloride can be produced by direct chlorination or oxychlorination of ethylene. These processes are typically used together in a balanced process which recycles HCl from vinyl chloride monomer production to the oxychlorination step. Oxychlorination can be based on air or oxygen. All the ethylene dichloride processes produce some carbon tetrachloride by-product, which is emitted from reactor vents, distillation column vents, fugitive process sources, liquid waste storage and waste incineration. Available information indicates that process vent controls exist or are planned at most plants. There are no current controls on process fugitives. Information is not available on existing or potential controls for the other carbon tetrachloride sources cited above.

There are four plants in the U.S. which produce perchloroethylene and/or trichloroethylene by chlorination or oxychlorination of ethylene dichloride. Two are in Texas, and two in Louisiana. Carbon tetrachloride formed in the initial reaction may be emitted from at least four process vents, from process fugitive sources, and from light ends storage. Available data on the processes and known emission controls at these plants indicate considerable variability between plants, but are not sufficient for detailed assessment.

Carbon tetrachloride is the major component of all major liquid grain fumigant formulations. From 60 to 80 percent carbon tetrachloride is present in these products, principally as a carrier and to reduce risks of fire and explosion. These fumigants are applied to grains during storage, transfer, milling, distribution and processing, at locations including on-farm storage, subterminal, terminal and port elevators, mill holding facilities and in transport vehicles. Emission of carbon tetrachloride from treated grain occurs during application and subsequent storage, turning, ventilation, loading, and further processing resulting in eventual loss of essentially all fumigant to the atmosphere. Possible measures for reduction of air emissions from fumigant use include expanded use of alternative fumigants and more efficient use of existing formulations. Additional emissions may occur in the mixing and packaging of fumigants, but no specific data are available.

Carbon tetrachloride is used as a solvent in the manufacturing of pharmaceutical products, which is typically done in small batch operations. Solvent emissions would be expected from all process components, especially dryers, reactors and distillation units, and from solvent storage and transfer. Specific locations are not available for manufacturers using carbon tetrachloride.

A number of other reported or potential sources of carbon tetrachloride air emissions were also identified during the data-gathering phase of the study. Carbon tetrachloride is apparently used as a scrubber absorbent in a phosgene production process at one or more phosgene/isocyanate/polyurethane plants. There are 15 phosgene production plants in the U.S., of which all but 2 small plants produce phosgene for captive use in isocyanate production. Potential emission points include storage and the scrubber vent.

Carbon tetrachloride has been identified as a solvent in production of several pesticides, including chlorothalonil, Linuron, and sulfuryl fluoride. Chlorothalonil is sold as Daconil, Forturf, Termil, and Bravo, and is produced at one plant in Texas. Linuron is a tradename for

N'-(3,4-dichlorophenyl)-N-methylurea, and is produced at a plant in Texas and one in Indiana. Sulfuryl fluoride, sold as Vikane, is produced at one plant in California.

One plant in Texas produces a vulcanizable elastomer called Hypalon®. This synthetic rubber is produced by reacting polyethylene with chlorine and sulfur dioxide in a solvent medium. Potential emission points for carbon tetrachloride solvent include storage, process vents, and the solvent recovery system.

Three plants in New York, Arkansas and Texas are reported to produce carbon tetrabromide by reacting carbon tetrachloride with aluminum tribromide. Storage, handling and process vents are the potential emission points at these locations. Carbon tetrabromide is a small-volume chemical for which production statistics are not available.

A carbon tetrachloride emission inventory for Texas also reported the following sources: a chlorine liquefaction operation, a resinous chlorowax production, a plant with symmetrical tetrachloropyridine and 4-amino-3,5,6-trichloropicalinic acid processes, and storage and loading at tank farms not owned by known carbon tetrachloride producers or users. An inventory for New Jersey reported carbon tetrachloride emission points related to several polymer productions and one dye production process. Other potential carbon tetrachloride sources which could not be verified include laboratory uses, metal cleaning, production of paint, adhesives, textiles, and embalming supplies.

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## 1.0 INTRODUCTION

### 1.1 OVERVIEW

This report provides preliminary information on sources of air emissions of carbon tetrachloride to assist EPA in regulatory decision-making. Potentially significant sources are identified and described, including carbon tetrachloride production, its use in chlorofluorocarbon (CFC) production, processes resulting in carbon tetrachloride by-product, and solvent and fumigant uses. Source descriptions include general information on each industry and production process, as well as emission estimates, applicable regulations and control technology.

In addition to source descriptions, this report also presents preliminary estimates of carbon tetrachloride emissions and control costs for carbon tetrachloride production plants and plants which produce CFC 11 and 12 from carbon tetrachloride. Methodology for this assessment is detailed in Section 1.2. Controlled emissions and control costs were estimated for two control options: Option 1 represents the baseline level of control which would be expected without further regulatory activity, and Option 2 consists of estimated best control (EBC) for each significant emission source.

The carbon tetrachloride emissions, control data, and costs of control in this report are based on information obtained from existing EPA reports and other published sources, from EPA data files on the synthetic organic chemical manufacturing industry, and from telephone contacts with control equipment vendors, and EPA, State and local agency personnel. This study did not include plant visits, source testing, or other original data gathering.

Chapter 2 describes physical properties of carbon tetrachloride relevant to its uses and emission control. A detailed listing of State regulations which may apply to sources of carbon tetrachloride

air emissions is also provided and control efficiencies are estimated where they are not prescribed in the regulations.

Chapters 3 through 6 contain process descriptions and estimates of emissions and control costs for the three types of carbon tetrachloride production processes and for production of CFC 11 and 12. Controlled emissions and control costs are estimated for control Options 1 and 2. Examples and details of emission and cost estimates are provided in Appendices A and B.

Chapters 7 through 10 provide information on other carbon tetrachloride source categories, including chemical production processes with carbon tetrachloride by-product, grain fumigant formulation and use, and pharmaceutical manufacturing. Each chapter includes a description of the source category, its carbon tetrachloride emission sources, and existing or feasible control technology.

## 1.2 SOURCE ASSESSMENT METHODOLOGY

This section describes the general methodology common to the source assessments for the three carbon tetrachloride production processes and CFC 11/12 production, which are presented in Chapters 3 through 6. Each chapter includes: (1) general information on production facilities and capacities, a process description and emission factors for a representative model plant for the process under consideration; (2) estimates of uncontrolled emissions; (3) identification of existing controls, current State regulations and Group III CTGs applicable to each plant, and estimates of Option 1 emissions based on the most stringent of these controls; (4) identification of estimated best controls and estimation of Option 2 emissions with these controls; and (5) estimation of control costs for each plant under Options 1 and 2. These areas are addressed individually below, followed by a brief discussion of the uncertainties involved in emission and cost estimates.

EPA reports and other published sources provide the information on plants, capacities and processes. Carbon tetrachloride emission factors were taken from a draft EPA report currently undergoing external review.<sup>1</sup> These emissions factors were based on all available data, including some emission sources which were documented for single plants. They include

factors for each identified source, including process vents, process fugitive emissions, storage, handling and secondary emissions. These factors and the emission and cost estimates in this report are based on representative model plants for each production process, which had been developed in a previous EPA study. These model plants include the elements common to documented production processes, assuming typical feedstocks, reaction types, purification and recycle steps, as well as typical storage facilities and process fugitive emission sources.

Emission factors were combined with production capacities of the respective model plants to estimate uncontrolled model plant emissions for each production process. Full-time operation was assumed to estimate process fugitive emissions. Uncontrolled emissions from each production process and related storage and loading were estimated from model plant emissions by assuming that emissions are directly proportional to carbon tetrachloride production. Emissions were adjusted to current production levels by assuming that all plants are operating at an industry-wide capacity utilization rate based on current national production and total production capacity. Production capacities are available for each carbon tetrachloride production location. Uncontrolled emissions for each process at the three locations with more than one production process were estimated using a typical distribution of capacities between processes which had been assumed for model plants in previous EPA studies. Available CFC production data consist of total CFC production capacities for each company, and a breakdown of recent national production of individual CFCs. Plant-specific CFC 11/12 production was estimated by assuming uniform distribution of capacities and CFC product mixes.

Existing controls at carbon tetrachloride and CFC 11/12 plants were identified through recent EPA surveys. Relevant State or local regulations were summarized for each plant. When possible, existing controls, applicability of regulations to specific plants, and appropriate control efficiencies were confirmed through contacts with State or local agencies. Where efficiencies for existing controls or regulations could not be obtained from these sources, preliminary engineering analyses were used to arrive at estimates. Existing draft Group III CTGs, related EPA documentation

and contacts with responsible EPA personnel were used to determine CTG control requirements which would be applicable to sources at carbon tetrachloride and CFC 11/12 plants. Option 1 emissions were estimated by applying the most stringent of these controls to estimated uncontrolled emissions. Option 2 emissions were estimated by applying EBC to uncontrolled emissions for each plant.

Capital and annual costs of Option 1 and 2 controls for each plant were estimated as follows. Detailed costs were developed for each controlled emission source at each model plant. These costs were based mainly on existing EPA cost estimates developed for general synthetic organic chemical manufacturing sources. In some cases, direct cost estimates were made by performing preliminary engineering assessments of controls for specific emission sources. Control costs for individual plants were estimated from model plant costs by assuming that costs are directly proportional to carbon tetrachloride or CFC 11/12 production. Emission reductions and product recovery credits in model plant cost analyses were derived by applying feasible control efficiencies to estimated uncontrolled emissions for each model plant emission source to which Option 1 or Option 2 controls apply. Since estimated model plant emissions were based on full production capacity, the emission reductions in model plant costs include an industry-wide capacity utilization factor. Where it was possible to estimate control of pollutants other than carbon tetrachloride by Option 1 and 2 controls, a separate model plant control cost analysis considering joint control of carbon tetrachloride and these other components is also provided. For consistency, however, model plant costs based on recovery of carbon tetrachloride alone were used in estimation of all plant-specific costs. The July 1982 price for carbon tetrachloride used in computing recovery credits is \$418/Mg (\$0.19/lb).<sup>2</sup> All control costs are also in July 1982 dollars, except where noted. Costs in original references were inflated to July 1982 using the Chemical Engineering plant cost index.<sup>3</sup> When estimation of capital and annual costs was necessary, cost factors cited in the original cost data reference were used on the assumption that they are more applicable than more general cost factors from other sources.

Due to the methods and data used to derive emissions and costs described above, the estimates made in the report should be considered preliminary. Critical assumptions are discussed below.

Use of model plant parameters did not allow consideration of variations between different production facilities. In reality no two plants are the same and several have been reported to vary from the model plants in ways that may affect the accuracy of emission and control cost estimates. Feedstocks, reaction types, purification steps, and in-plant recycle are some of the variables that have been documented. Emission data used in emission factor development often were obtained from single plants, and may not apply to all production processes. The relative volume and type of storage capacity and storage/loading throughputs and associated emissions and costs may vary considerably from the model plant assumptions. For example, proximity of carbon tetrachloride plants to CFC 11/12 plants can affect the amount of carbon tetrachloride storage, loading and transportation necessary, since transfers may be made directly by pipeline.

The accuracy of emission and cost estimates is further dependent on assumptions regarding capacity utilization, and on the correct distribution of production capacities at two-process carbon tetrachloride plants, at plants producing a variety of CFCs, and between various plants for which only company-wide total CFC capacity is known. Some of these assumptions may not affect the accuracy of emission and control cost estimates at the plant or national level, but the cumulative effects of individual assumptions could not be addressed in detail.

In most cases, existing control costs were used as the basis of estimates in this preliminary analysis. Some uncertainty is involved in deriving carbon tetrachloride-specific costs from costs developed for general synthetic organic chemical manufacturing sources and extrapolating from costs for other source types. This uncertainty is due mainly to lack of sufficient information on the emission sources, and the assumptions which had to be made in applying existing cost estimates to the specific cases of interest. In some cases, direct cost estimates were made by performing preliminary engineering assessments of controls for specific emission sources. These estimates also entail considerable uncertainty due

to the limited technical data available and the tentative nature of the engineering and cost analyses. In some cases, control cost estimates may be somewhat underestimated because they were based on costs for new equipment rather than retrofit controls. Expenses such as remote utility connection and ducting and piping for vapor recovery and recovered product were based on standardized installation cost factors. Site-specific factors which would add to the estimated base control costs were neglected, since plant-specific data which would allow explicit consideration of these potential cost variations were not available. Thus the costs presented should be considered rough estimates (i.e. +50 percent).

### 1.3 REFERENCES

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## 2.0 CARBON TETRACHLORIDE PROPERTIES AND REGULATIONS AFFECTING EMISSIONS

This chapter is divided into two sections: Section 2.1 describes the physical properties of carbon tetrachloride; Section 2.2 presents existing and anticipated regulations affecting emissions of carbon tetrachloride from various sources.

### 2.1 PROPERTIES OF CARBON TETRACHLORIDE

Carbon tetrachloride,  $\text{CCl}_4$ , is a clear, colorless, nonflammable liquid at normal temperatures and pressures. Physical properties of carbon tetrachloride are presented in Table 2-1.

Carbon tetrachloride is miscible with most organic solvents, but is essentially insoluble in water. It is a powerful solvent for asphalt, benzyl resin (polymerized benzyl chloride), bitumens, chlorinated rubber, ethyl cellulose, fats, gums, resin, and waxes.<sup>1</sup> It is relatively volatile, with a vapor pressure of 11.94 kPa (90 mm Hg, 1.74 psi) at 20°C. Figure 2-1 shows the vapor pressure of carbon tetrachloride as a function of temperature in the range of available condenser control systems.

Due to its high thermal capacity, carbon tetrachloride increases the lower explosion limits of gaseous mixtures and has an extinctive effect on flames. The density of carbon tetrachloride vapor is over five times that of air; thus, in cases where concentrated gaseous emissions occur, the plume will tend to settle to the ground before dispersing into the ambient air.<sup>2</sup>

Carbon tetrachloride decomposes to phosgene at high temperatures. Thermal decomposition occurs very slowly at temperatures up to 400°C (750°F). At temperatures of 900 to 1300°C (1650 to 2370°F), extensive dissociation occurs to form perchloroethylene, hexachloroethane and some chlorine. Reaction of carbon tetrachloride with steam at high temperatures results in the formation of chloromethanes, hexachloroethane, and perchloroethylene.<sup>1</sup>

TABLE 2-1. PHYSICAL PROPERTIES OF CARBON TETRACHLORIDE,  $\text{CCl}_4$ <sup>1</sup>

Property	Value
Synonyms: Tetrachloromethane, methane tetrachloride, perchloromethane, benzinoform	
Molecular weight	153.82
Melting point, °C	-22.92
Boiling point, °C	76.72
Refractive index, 15°C	1.46305
Specific gravity	
20/4°C	1.59472
Autoignition temperature, °C	>1,000
Flash point, °C	None
Vapor density, air = 1	5.32
Surface tension, mN/m(=dyn/cm)	
0°C	29.38
20°C	26.77
60°C	18.16
Specific heat, J/kg	
20°C	866
30°C	837
Critical temperature, °C	283.2
Critical pressure, MPa	4.6
Critical density, kg/m <sup>3</sup>	558
Thermal conductivity, mW/(m·K)	
Liquid, 20°C	118
Vapor, bp	7.29
Average coefficient of volume expansion, 0-40°C	0.00124
Dielectric constant	
Liquid, 20°C	2.205
Liquid, 50°C	1.874
Vapor, 87.6°C	1.00302

CONTINUED

TABLE 2-1. (continued)

Property	Value
Heat of formation, kJ/mol	
Liquid	-142
Vapor	-108
Heat of combustion, liquid, at constant volume, 18.7°C, kJ/mol	365
Latent heat of fusion, kJ/mol	2.535
Latent heat of vaporization, kJ/kg	194.7
Viscosity, 20°C, mPa·s	0.965
Vapor pressure, kPa	
0°C	4.410
20°C	11.94
40°C	28.12
60°C	58.53
150°C	607.3
200°C	1,458
Soly of CCl <sub>4</sub> in water, 25°C, g/100 g H <sub>2</sub> O	0.08
Soly of water in CCl <sub>4</sub> , 25°C, g/100 g CCl <sub>4</sub>	0.013

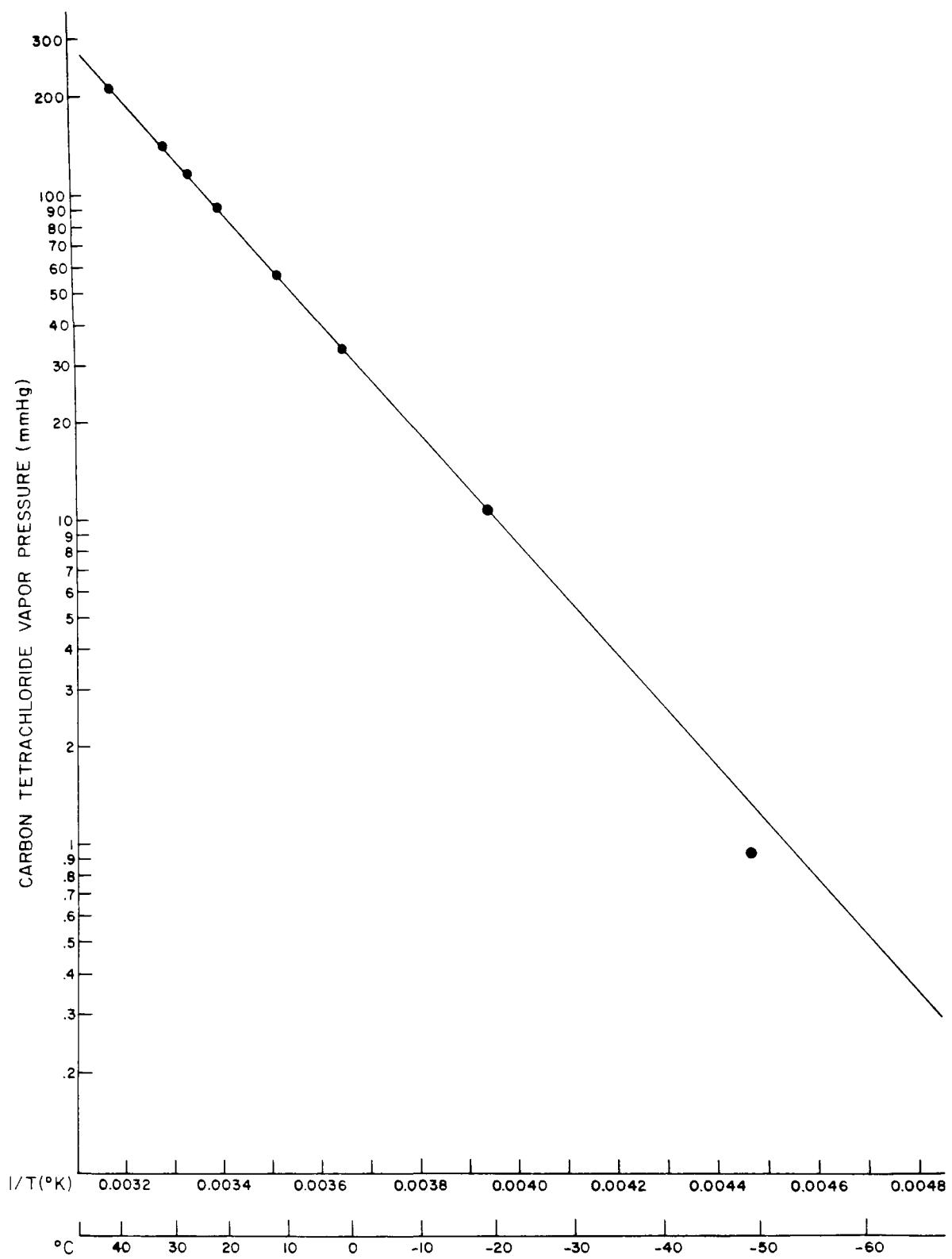


Figure 2-1. Vapor pressure of carbon tetrachloride.<sup>1,2</sup>

Carbon tetrachloride is relatively stable in the atmosphere, with various recent estimates of its atmospheric lifetime ranging from 18 to 100 years. Ultraviolet photolysis in the stratosphere has been proposed as the dominant atmospheric removal mechanism. The major product of this reaction is phosgene. Reaction with oxygen radicals may also account for some removal. Due to uncertainties in overall tropospheric levels, cumulative world emissions and removal rates, there is some disagreement as to the existence of significant natural sources of carbon tetrachloride. However, a number of recent studies suggest that atmospheric levels can be attributed directly to anthropogenic emissions.<sup>2</sup>

## 2.2 REGULATIONS AFFECTING EMISSIONS OF CARBON TETRACHLORIDE

Current and anticipated regulations which may affect existing sources of carbon tetrachloride emissions include State regulations for volatile organic compounds (VOC) and toxic substances. In addition, there are several EPA Control Techniques Guidelines (CTGs) which will affect carbon tetrachloride sources when adopted in areas requesting ozone National Ambient Air Quality Standard attainment date extensions beyond 1982. Control requirements are described individually below, and corresponding control efficiencies are summarized in tabular form. It should be noted that the actual applicability of a given regulation to a specific source can be influenced by a number of variables (location, size, type of operation, etc.) The applicability of specific regulations to individual plants is discussed in the chapters dealing with specific source categories.

### 2.2.1 Existing State Regulations

State regulations applicable to carbon tetrachloride production facilities and processes in which carbon tetrachloride is a feedstock or by-product are summarized in this subsection on a State-by-State basis. Regulations applicable to the use of carbon tetrachloride as a solvent are not included. Requirements which are not relevant to carbon tetrachloride were also omitted, such as those applying to VOC which do not include carbon tetrachloride (gasoline, crude oil, etc.). Detailed specifications for floating roof VOC storage tanks were not summarized because refrigerated

condensers are the dominant control for carbon tetrachloride. Control efficiencies for carbon tetrachloride were either taken from the regulations or estimated when not specified in the regulation. The applicable definition of VOC as related to carbon tetrachloride is provided for each State.

In cases where carbon tetrachloride is not subject to regulation solely due to the definition of affected compounds, regulations are cited to allow assessment of the impact of revision of the definition or regulatory interpretation to include carbon tetrachloride.

#### ALABAMA

Section 6.3 of the Alabama Air Pollution Rules, Loading and Storage of VOC, is the only regulation which applies to the Stauffer carbon tetrachloride plant at LeMoyne, Alabama. This statute requires:

1. VOC storage tanks over 1,000 gallons must be a pressure tank or be equipped with one of the following:

- a. submerged fill pipe,
- b. external or internal floating roof,
- c. vapor recovery system, or
- d. other equipment or means of equal efficiency.

2. Loading of tanks, trucks or trailers from terminal or bulk storage must use the following:

- a. vapor collection and disposal system, or loading system allowing 95 percent submerged fill, or equivalent,
- b. prevention of liquid drainage from the loading device, and
- c. vapor-tight and automatic-closing loading line connectors unless hatch-loaded.

Submerged fill is the minimum requirement in both these regulations. Since submerged fill is part of the baseline case in available emission factors, the Alabama storage and loading regulations have been assumed to provide no additional emission control.

Definition: "'Volatile organic compound' (also denoted as VOC) means any organic compound excluding methane, ethane, 1,1,1-trichloroethane (methyl chloroform) and trichlorotrifluoroethane with a true vapor pressure of 1.5 psia under a storage condition."

## ARKANSAS

The carbon tetrabromide plant at El Dorado is not subject to any limits which affect carbon tetrachloride emissions.

Definition: "'Volatile Organic Compound' (VOC) means any compound of carbon that has a vapor pressure greater than 0.1 millimeters of mercury at standard conditions excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonates. The term includes hydrocarbons controlled by new source standards of performance, and by the national ambient air quality standards."

Exemptions: Methane, ethane, 1,1,1-trichloroethane, methylene chloride, CFC-11, CFC-12, CFC-22, CFC-23, CFC-113, CFC-114, and CFC-115.

## CALIFORNIA<sup>4</sup>

### Bay Area Air Quality Management District (BAAQMD)

1. Regulation 8, Rule 5 - Storage of Organic Liquids requires that organic liquid storage tanks between 260 gallons and 40,000 gallons must be equipped with a submerged fill pipe or equivalent device. Tanks over 40,000 gallons, other than pressure tanks, must have either an external floating roof with secondary seal, an equivalent internal floating roof, a vapor recovery system of 95 percent efficiency or other control of 95 percent efficiency. See Organic Liquid definition, below.

2. Regulation 8, Rule 22 - Valves and Flanges at Chemical Plant Complexes applies to organic compounds, and requires annual inspection and repair or minimization of 10,000 ppm (as methane) leaks within fifteen days, depending on whether the valve or flange is essential. Essential valve leaks must be repaired at the next scheduled turnaround but no longer than six months later than discovered. Any unit exceeding 75,000 ppm (as methane) must be repaired within fifteen days.

Rule 22 is assumed to provide negligible control of fugitive emissions. This assumption is based on coverage of only valves and flanges, with no control of pumps or compressors, and ineffectiveness of annual as opposed to quarterly monitoring, as shown for SOCMI valves in EPA assessment of various monitoring intervals.<sup>5</sup>

3. There are no BAAQMD rules for loading or process controls which would apply to carbon tetrachloride.

Definitions: Organic Liquids (Regulation 8, Rule 1): "All organic compounds containing hydrogen and which would exist as liquids at actual conditions of use or storage." Since carbon tetrachloride does not contain hydrogen, Rule 5, above, would not apply to carbon tetrachloride storage tanks.

Organic Compound (Regulation 8, Rule 22): "Any compound of carbon (excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, ammonium carbonate and methane). If the person responsible for an emission of organic compounds can demonstrate that the emission contains ethane and the emission would not be in violation of the requirements of this Rule if the ethane were not present, then that emission shall not be considered a violation of this Rule."

#### South Coast Air Quality Management District

The Allied CFC plant at El Segundo must meet the following requirements:

1. Rule 463 - Storage of Organic Liquids requires tanks over 39,630 gallons to be pressure tanks or be equipped with one of the following:

- a. an external floating roof,
- b. a fixed roof with internal-floating-type cover,
- c. a vapor recovery system with 95 percent control efficiency, or
- d. other equipment with 95 percent control efficiency.

2. Rule 466 - Pumps and Compressors requires seals or other devices of equal efficiency, maintained to prevent: (a) leakage of more

than three drops per minute, (b) visible liquid mist or vapor and (c) any visible indication of leakage at or near the shaft/seal interface of gas compressors. Pumps and compressors leaking over 10,000 ppm VOC must be repaired or replaced at the next scheduled process turnaround, with interim requirements depending on availability of operable spare units. Visual inspections are required daily, once every 8 hours for units within 3 miles of a continuously manned control center. Hydrocarbon detection instrument inspections are required annually for pumps, and quarterly for compressors. Exemptions include units which have drivers with less than one horsepower, which operate over 260<sup>0</sup>C, which are vented to an emission control system, which handle liquids or gases with VOC content of 20 percent or less, and which have dual seals.

Rule 466.1 - Valves and Flanges requires annual inspection of valves and flanges at chemical plants, repair of leaks exceeding three drops per minute of liquid VOC or 10,000 ppm of gaseous VOC, and re-inspection of valves after repair. Valves at the ends of open-ended lines must be sealed with a blind flange, plug, or cap when not in use, except for sampling lines, safety valves and bleeder valves in double block and bleeder valve systems.

Rule 467 - Safety Relief Valves prohibits use of safety pressure relief valves at pressures over 776 mm Hg absolute pressure, unless the valve is vented to a vapor recovery or disposal system, protected by a rupture disk, or maintained by an approved inspection system.

Rules 466, 466.1, and 467 are essentially equivalent to the SOCMF fugitive CTG, discussed in 2.2.2, which is estimated to provide about 42 percent control of fugitive emissions.

Definition: "Volatile Organic Compounds are compounds of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, ammonium carbonate, ethane, methane, 1,1,1-trichloroethane, methylene chloride, and trichlorotrifluoroethane, that have a Reid vapor pressure (RVP) greater than 80 mm Hg (1.55 pounds per square inch), or an absolute vapor pressure (AVP) greater than 36 mm Hg (0.7 psi) at 20<sup>0</sup>C."

ILLINOIS

Rule 205 (Organic Material Emission Standards and Limitations) includes the following regulations which would apply to any relevant carbon tetrachloride sources.

1. Storage: Tanks for volatile organic material (VOM) over 40,000 gallons must be a pressure tank or be equipped with:

- a. a floating roof,
- b. a vapor recovery system capable of 85 percent collection of VOM and a disposal system which prevents further emission to the atmosphere, or
- c. equipment or means of equal efficiency.

2. Loading:

- a. Facilities loading greater than 40,000 gallons per day into trucks or trailers must use submerged loading or equally effective control. Otherwise, emissions must be restricted to less than 8 pounds per hour.
- b. Loading into stationary tanks over 250 gallons must be done with a permanent submerged loading pipe or equivalent, unless it is a pressure tank or a vapor recovery system is used.

Since submerged loading is part of the baseline case in available emission factors, these loading requirements are assumed to provide no additional control.

3. Pumps and Compressors: No unit may discharge over two cubic inches of liquid VOM in any 15-minute period. This is equivalent to standard industry practice, and provides no additional emission control.

4. Waste Gas Disposal: Any waste gas stream from any petroleum or petrochemical manufacturing process must be limited to 100 ppm equivalent methane. Alternatively, existing sources (as of January 1, 1977) can elect to comply with the limits cited for use of organic material, which prohibit discharge of more than 8 pounds of organic material per hour unless emissions are controlled by a system with 85 percent efficiency.

Definitions: "Organic Material: Any chemical compound of carbon including diluents and thinners which are liquids at standard conditions and which are used as dissolvers, viscosity reducers or cleaning agents, but excluding methane, carbon monoxide, carbonic acid, metallic carbonic acid, metallic carbide, metallic carbonates, and ammonium carbonate."

"Organic Vapor: Gaseous phase of an organic material or a mixture of organic materials present in the atmosphere."

## KANSAS

VOC regulations in Kansas apply only to surface coating, gasoline and other petroleum liquids and cutback asphalt.

Definition: "Volatile organic compounds (VOC) means any carbon compound having a vapor pressure greater than 0.1 mm of mercury at standard conditions excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate. For the purposes of the regulation, methane; ethane; methylene chloride; 1,1,1-trichloroethane (methyl chloroform) and trichlorotrifluoroethane (fluorocarbon 113) shall not be considered to be volatile organic compounds."

## KENTUCKY

Kentucky's existing source regulations for VOC storage and loading apply only to "petroleum liquids" and/or gasoline, and do not cover carbon tetrachloride. Regulations for existing process gas streams only cover hydrogen sulfide, sulfur dioxide and carbon monoxide.

Definition: Existing source VOC regulations in Kentucky use the following definition: "'Volatile organic compounds' means chemical compounds of carbon (excluding methane, ethane, carbon monoxide, carbon dioxide, carbonic acid, metallic carbides, and ammonium carbonate) which have a vapor pressure greater than one-tenth (0.1) mm Hg at conditions of twenty (20) degrees Celsius and 760 mm Hg."

## LOUISIANA

Although carbon tetrachloride is not covered by the Louisiana definition of VOC, given below, the State agency considers sources of carbon tetrachloride in Louisiana to be subject to their VOC regulations, which include the following requirements:

1. VOC storage tanks over 40,000 gallons which are not pressure tanks must have a submerged fill pipe and one of the following controls:

- a. internal or external floating roof,
- b. a vapor loss control system equivalent to floating roof, or
- c. other equivalent equipment or means.

This is assumed to be equivalent to the Group III CTG for VOL storage, which gives 95 percent control (see 2.2.2).

2. VOC storage tanks between 250 and 40,000 gallons must have one of the following controls:

- a. submerged fill pipe,
- b. vapor recovery system, or
- c. other equivalent equipment or means.

This is equivalent to standard industry practice, providing no additional control.

3. VOC loading facilities with daily throughput of 40,000 gallons or more must have vapor collection and disposal, or an equivalent, and spill prevention for the filling equipment. Barge and ship loading is exempt. The State agency interprets and enforces this regulation as a 90 percent control requirement.<sup>6</sup>

4. Pumps, compressors, valves, etc. must be equipped with mechanical seals or equivalent equipment or means. Best practical housekeeping and maintenance practices are also required. This is equivalent to standard industry practice.

5. Halogenated hydrocarbon waste gases must be burned and their combustion products controlled to an acceptable level (not specified). Other methods of control may be substituted, such as carbon adsorption, refrigeration, catalytic and/or thermal reaction, secondary steam stripping, recycling or vapor recovery system. This requirement can be waived for sources less than 100 tons per year, for gases which will not support combustion or if disposal cannot be accomplished without causing economic hardship. As discussed in 2.2.2, below, thermal oxidation is generally capable of 98 percent control, or 20 ppmv, whichever is more stringent. The other permitted substitutes are generally not capable of control at this level, however, and specific acceptable level of control would depend on the characteristics of the emissions in question.

Definition: "Any compound containing carbon and hydrogen or containing carbon and hydrogen in combination with any other element which has a vapor pressure of 1.5 pounds per square inch absolute (77.6 millimeters of mercury) or greater under actual flow or storage conditions."

Exemptions: Methane, ethane, 1,1,1-trichloroethane (methyl chloroform), methylene chloride, dichlorodifluoromethane, chlorodifluoromethane, trifluoromethane, dichlorotetrafluoroethane, trichlorotrifluoroethane, chloropentafluoroethane.

## MICHIGAN

Part 6 of Michigan's air pollution control rules includes the following controls which would apply to storage or loading of carbon tetrachloride.

1. R336.1604 Storage of Organic Compounds requires storage tanks over 40,000 gallons to be pressure tanks, or have either
  - a. a floating roof, or
  - b. a vapor recovery system, or equivalent, with 90 percent control efficiency.

2. R336.1609 Loading Existing Delivery Vessels with Organic Compounds requires that all loading facilities handling over 5,000,000 gallons per year have:

- a. submerged loading for facilities outside of ozone nonattainment areas,
- b. vapor recovery such that emissions are less than 0.7 pounds of organic vapor per 1000 gallons of organic compounds loaded, in nonattainment areas.

Delivery vessels (tank trucks, trailers, railroad tank cars or any similar vessel) loaded at facilities subject to (b), above, must be equipped with vapor collection system interlocks, drainage prevention, and vapor-tight fittings.

Submerged loading provides no control over the baseline case in uncontrolled emission factors. The vapor recovery requirement in (b) would result in approximately 80 percent control over the estimated 0.24 kg/Mg emission factor for handling at carbon tetrachloride production facilities, presented in Tables 3-2, 4-1 and 5-1.

Definition: "Volatile organic compound means any compound of carbon or mixture of such compounds, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, boron carbide, silicon carbide, ammonium carbonate, ammonium bicarbonate, methane, and ethane, that has a vapor pressure of more than 0.1 millimeters of mercury at standard conditions."

#### NEW JERSEY

New Jersey volatile substances rules include the following requirements which would apply to storage and loading of carbon tetrachloride.

1. 7:27-16.2 Storage of Volatile Organic Substances requires that carbon tetrachloride storage tanks over 300,000 gallons be controlled with an external or internal floating roof with at least one tight seal. The minimum affected tank size is based on the vapor pressure of the VOS stored. For these tanks, control is estimated to be 95 percent, equivalent to the VOL storage CTG, discussed in 2.2.2.

2. 7.27-16.3 Transfer Operations requires submerged filling or equivalent control in transfer of volatile organic substances into any vessel over 2,000 gallons (marine vessels exempted). This provides no additional emission control over the assumed baseline.

3. 7:27-16.6 Source Operations other than Storage Tanks, Transfers, etc., (a) establishes a sliding scale for control of VOS emissions not controlled by other rules. This scale is based on the concentration and vapor pressure of the VOS, and the effective control required or possible exclusion for low emission rates must be based on data for the specific source in question.

Paragraph (d) of this section prohibits leakage of VOS from flanges, manholes, and other non-moving joints and fittings. Paragraph (e) prohibits leakage from valves, pumps, and compressors resulting in concentration over 10,000 ppm by volume measured at 1 centimeter, or if emissions are in the liquid state. Since these paragraphs do not specify inspection intervals and repair requirements, it is assumed that their effective control of fugitive emissions is marginal (0 percent).

Definition: "Volatile organic substances, herein abbreviated as VOS, means any organic substances, mixture of organic substances, or mixture of organic and inorganic substances including, but not limited to petroleum crudes, petroleum fractions, petrochemicals, solvents, diluents, and thinners which have vapor pressures or sums of partial pressures of organic substances of 0.02 pounds per square inch (1 millimeter of mercury) absolute or greater measured at standard conditions; and, in the case of surface coating formulations, includes any coalescing or other agent, regardless of vapor pressure, which evaporates from the coating during the drying phase; but does not include methane, trichlorofluoromethane, dichlorodifluoromethane, chlorodifluoromethane, trifluoromethane, 1,1,2-trichloro-1,2,2-trifluoroethane, 1,2-dichloro-1,1,2,2-tetrafluoroethane, and chloropentafluoroethane."

New Jersey toxic substances rules (NJAC 7:37-17) require registration of carbon tetrachloride emissions and control "at a rate or concentration equivalent to advances in the art of control" for the type of emission

involved. Discharge of toxic volatile organic substances (including carbon tetrachloride) must be no less than 40 feet above grade, 20 feet above areas of human use or occupancy and directed upward at a velocity of 3,600 feet per minute or greater. Emissions of less than 0.1 pounds per hour are exempt. Control efficiencies under these rules are determined on a case-by-case basis, depending on the characteristics of each affected source.

These rules apply to the following "toxic volatile organic substances."

Benzene (Benzol)  
Carbon tetrachloride (Tetrachloromethane)  
Chloroform (Trichloromethane)  
Dioxane (1,4-Diethylene dioxide)  
Ethylenimine (Aziridine)  
Ethylene dibromide (1,2-Dibromethane)  
Ethylene dichloride (1,2-Dichloroethane)  
1,1,2,2-Tetrachloroethane (sym Tetrachloroethane)  
Tetrachloroethylene (Perchloroethylene)  
1,1,2-Trichloroethane (Vinyl trichloride)  
Trichloroethylene (Trichloroethene)

#### NEW YORK

Part 212 of the New York State Pollution Control Regulations applies to processes and exhaust and/or ventilation systems not regulated by other specific rules. Application of this rule requires an "environmental rating" of the pollutant involved, which is issued when a permit is applied for. Depending on this rating and the emission rate potential of the source, a look-up table provides the degree of control required. Regulations do not exist for VOC emissions from fugitive SOCMi sources, storage, or loading.

Definition: "Volatile Organic Compound (VOC). Any compound of carbon excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, that has a vapor pressure greater than 0.10 mm (0.0039 inches) of Hg at a temperature of 20°C (68°F and a pressure of 760 mm (30 inches) of Hg."

New York's toxic pollutant control scheme is based on a policy document ("Air Guide 1"), which serves as guidance to the State agency's regional offices in their regular permit review process. This policy has not been made part of the New York State Pollution Control Regulations. It establishes three toxicity categories with varying control requirements. Carbon tetrachloride is in the "high toxicity" category, which requires best available control technology for sources emitting over 1 pound per hour. In addition, 0.0167 ppm is used as an acceptable ambient limit, based on modeling of the ambient concentration attributable to the source. This number is derived by dividing the ACGIH Threshold Limit Value (TLV) of 5 ppm by a safety factor of 300.<sup>7,8</sup> Since determination of best available control technology is source-dependent, generalized estimates of control efficiencies are not possible under Air Guide 1.

## TEXAS

Texas has two sets of VOC regulations which apply in attainment/unclassified counties and nonattainment counties, respectively. For sources related to carbon tetrachloride, requirements for VOC loading and unloading and for VOC vent gas streams are the same in all counties, and only VOC storage requirements differ, as described separately below. The following definitions apply throughout.

Definitions: "Vapor Recovery System. Any control system that reduces volatile organic compounds (VOC) emissions such that the aggregate partial pressure of all VOC vapors will not exceed a level of 1.5 psia (10.3 kPa) or other emission limits specified in Chapter 115 of this title (relating to Volatile Organic Compounds)."

"Volatile Organic Compound (VOC). Any compound of carbon or mixture of carbon compounds, excluding methane, ethane, methyl chloroform, Freon 113, carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate."

1. VOC Vent Gas Streams: VOC vent gas stream control requirements do not include carbon tetrachloride in the list of affected compounds and classes of compounds, but the list does include ethylene and other

compounds which may occur in vent gases from some carbon tetrachloride production processes and processes involving carbon tetrachloride as a byproduct. In Texas nonattainment counties, ethylene dichloride processes appear to be the only relevant sources. Vent gases must be "properly burned at a temperature equal to or greater than 704°C (1300°F) in a smokeless flare or a direct-flare incinerator," or controlled by approved alternate means. Sources emitting less than 100 lbs/day of combined affected VOC or less than 250 lbs/hr of a combined VOC with vapor pressure less than 0.44 psia are exempt. Control efficiencies must be estimated on a case-by-case basis due to variability in vent stream combustibility.

Compounds regulated under this rule include: ethylene, butadiene, isobutylene, styrene, isoprene, propylene, alpha-methyl-styrene, aldehydes, alcohols, aromatics, ethers, olefins, peroxides, amines, acids, esters, ketones, sulfides, and branched chain hydrocarbons (C8 and above).

2. VOC Loading and Unloading: VOC loading and unloading facilities with average throughputs of 20,000 gallons or more per day must have a vapor recovery system, vapor-tight seal, and drainage control (ship and barge loading facilities are exempt).

3. VOC Storage in Attainment/Unclassified Counties: The following requirements apply to the DuPont plant at Corpus Christi, which is actually in Ingleside, San Patricio County. Sources there include production of carbon tetrachloride and chlorofluorocarbons. All other carbon tetrachloride sources under consideration are covered by the storage rules for nonattainment counties, below.

- a. VOC storage tanks over 25,000 gallons must be a pressure tank or be equipped with an internal or external floating roof, or a vapor recovery system.
- b. VOC storage tanks over 1,000 gallons must be a pressure tank or be equipped with a submerged fill pipe or vapor recovery system.

4. VOC Storage in Nonattainment Counties: The following storage regulations apply to VOCs in the vapor pressure range of carbon tetrachloride and related halogenated compounds unless stored in pressurized tanks.

- a. VOC storage tanks between 1,000 and 25,000 gallons must have a submerged fill pipe.
- b. VOC storage tanks between 25,000 gallons and 42,000 gallons must have an internal or external floating roof (any type) or a vapor recovery system.
- c. VOC storage tanks over 42,000 gallons must have either an internal floating roof, external floating roof with vapor-mounted primary seal and secondary seal, or a vapor recovery system.

It is estimated that the storage and loading controls cited above will provide about 50 percent control of carbon tetrachloride emissions.

This estimate is based on the 1.5 psi vapor pressure requirement for vapor recovery systems, the vapor pressure reduction necessary to meet this requirement from an ambient temperature of 30°C (86°F) and vapor pressure of 2.9 psi, and an assumed control proportional to vapor pressure reduction.

#### WEST VIRGINIA

There are no regulations that apply to sources of carbon tetrachloride in West Virginia.

#### SUMMARY

Table 2-2 provides a summary of existing State regulations for VOC which apply to carbon tetrachloride sources. Cited control efficiencies and control requirements which can not be assigned specific control efficiencies are discussed in the state-by-state listings, above. This tabulation for VOC does not include the toxics regulations for New Jersey and New York, described above, which are currently in the process of implementation. The New Jersey regulation requires control "at a rate or concentration equivalent to advances in the art of control," and specifies height and velocity of discharges. New York requires best available control technology and modeling of acceptable source attributed ambient levels. For carbon tetrachloride the acceptable level is 0.0167 ppm.

TABLE 2-2. ESTIMATED CONTROL EFFICIENCIES FOR STATE VOC REGULATIONS

State	Control efficiencies (percent)			
	Process	Fugitive	Storage	Loading
Alabama	NR	NR	0	0
Arkansas	NR	NR	NR	NR
California				
Bay Area	NR	0	95 <sup>a</sup>	NR
South Coast	NR	42	95 <sup>a</sup>	NR
Illinois	NE	0	85	0
Kansas	NR	NR	NR	NR
Kentucky	NR	NR	NR	NR
Louisiana	NS	0	95 <sup>a</sup>	90
Michigan	NR	NR	90 <sup>a</sup>	NE
New Jersey	NE	0	95 <sup>b</sup>	0
New York	NE	NR	NR	NR
Texas				
Attainment/ Unclassified	NE	NR	50	50
Nonattainment	NE	NR	50	50
West Virginia	NR	NR	NR	NR

<sup>a</sup>Tanks over 40,000 gallons only. Smaller tanks have negligible control.

<sup>b</sup>Tanks over 300,000 gallons only. Smaller tanks have negligible control.

NE = No typical control efficiency can be assumed, source-specific determination necessary. See text for specific requirements.

NR = No regulation applicable to carbon tetrachloride emissions.

NS = Level of control not specified.

0 = Regulation equivalent to no control. These typically represent standard operating practice or the baseline case in emission factor development.

## 2.2.2 Group III Control Techniques Guidelines

It is anticipated that ozone nonattainment areas which have received extensions beyond 1982 will be required to adopt all Group III CTGs. These CTGs were therefore reviewed for applicability to known sources of carbon tetrachloride. Two Group III CTGs (covering volatile organic liquid storage and fugitive emissions from synthetic organic chemical, polymer and resin manufacturing) would apply to operations in post-1982 attainment-date areas which store carbon tetrachloride, use it as a feedstock, or produce it as a principal product, co-product, by-product or intermediate. The requirements and anticipated control efficiencies of these CTGs are discussed individually below.

The Group III CTG for control of VOC emissions from air oxidation processes in the synthetic organic chemical manufacturing industry also applies to one potential by-product source of carbon tetrachloride, the production of ethylene dichloride by oxychlorination. While it does not apply to the current source assessments, it is discussed below for possible future reference.

### Volatile Organic Liquid (VOL) Storage<sup>9</sup>

The June 1981 draft CTG for VOL storage applies to fixed-roof and floating roof storage tanks with capacities of 40,000 gallons or more which store VOL with vapor pressure of 1.5 psia or greater at storage conditions. The principal controls discussed and analyzed in the CTG are internal and external floating roofs. Add-on vapor control systems for fixed-roof tanks are also mentioned as alternate control techniques, including those using carbon adsorption, refrigerated vent condensers, absorbers and oxidation units for recovery or destruction of the VOC. Of these choices, refrigerated condensers appear to be the most likely choice for control of carbon tetrachloride storage. As indicated in Chapters 3, 4, and 5, refrigerated condensers are the only storage control known to be currently in use at carbon tetrachloride production plants. There is apparently one floating roof in use at a chlorofluorocarbon

production plant.<sup>10</sup> Industry sources have indicated that floating roofs are not recommended for carbon tetrachloride service due to its tendency to degrade floating roof seal components.<sup>11</sup>

The reasonably available control technique (RACT) requirement in this CTG is based on equipment specifications rather than a specific control efficiency, which complicates estimation of a control effectiveness. The June 1981 draft CTG cites control efficiencies of 93 to 98 percent for the various floating roofs which would qualify as RACT in that draft.<sup>12</sup> For the purposes of this analysis, it is assumed that 95 percent control will be acceptable for equivalency to RACT. This level of control appears achievable with refrigerated condensers of adequate design and cooling capacity. For example, Dow Chemical permit applications<sup>13</sup> and 114 letter responses<sup>14</sup> both indicate 95 percent control of carbon tetrachloride storage emissions at Freeport, Texas, with refrigerated condensers operating at -20°C outlet temperatures. A feasible control range of 90 to 95 percent for carbon tetrachloride, with this outlet temperature, is also supported by the assessment of refrigerated condensers for SOCMI storage performed by IT Enviroscience.<sup>15</sup>

#### VOC Fugitive Emissions<sup>16</sup>

The August 1981 draft CTG for VOC fugitive emissions from synthetic organic chemical, polymer and resin manufacturing equipment applies to pumps, compressors, in-line process valves, pressure relief devices, open-ended valves, sampling connections, flanges, agitators and cooling towers. RACT would consist of a quarterly leak detection and repair program and capping of open-ended lines. Some alternative control strategies would be possible for valves only, including an "allowable percentage of valves leaking" approach and skip-period monitoring. RACT is estimated to achieve an overall emission reduction of 42 percent for all model units.<sup>17</sup> Exemptions would be provided for unsafe and difficult-to-reach components, and for plants producing less than 1,000 Mg per year of any of the SOCMI chemicals listed in Appendix B of the CTG.<sup>16,17</sup> It is not expected that these exemptions will have a significant effect on CTG emission reductions at carbon tetrachloride plants or chlorofluorocarbon production facilities.

## VOC Emissions from Air Oxidation<sup>18</sup>

The June 1981 draft CTG for VOC emissions from SOCMI air oxidation applies to production of a total of 36 chemicals by air oxidation. Of these, only production of ethylene dichloride (1,2-dichloroethane) is known to result in a small percentage of by-product carbon tetrachloride.<sup>19</sup> The CTG considers thermal oxidation the only universally-applicable control technique for air oxidation processes, but cites both thermal oxidation and catalytic incineration as being used on one or more ethylene dichloride production processes. Condensation and absorption are also cited as being in use for product or raw material recovery at ethylene dichloride plants. RACT is based on thermal oxidation, at a control efficiency of 98 percent or 20 ppmv exit concentration, whichever is less stringent, for all streams having a total resource-effectivness (TRE) index value of less than 2.9. (TRE is a measure of the supplemental total resource requirement per unit VOC reduction by thermal incineration, including supplemental fuel, capital, labor, electricity, and water and caustic for control of offgas containing halogenated compounds.)

## 2.3 REFERENCES

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### 3.0 CARBON TETRACHLORIDE PRODUCTION WITH PERCHLOROETHYLENE CO-PRODUCT

This chapter discusses plants which co-produce carbon tetrachloride and perchloroethylene, by chlorinolysis or chlorination of hydrocarbon feedstocks. A brief process description is followed by estimates of uncontrolled emissions, Option 1 and Option 2 controlled emissions, and associated control costs. A number of plants manufacture carbon tetrachloride by the perchloroethylene co-product process as well as by the methane chlorination process (which is discussed in Chapter 4). This chapter addresses a number of assumptions and related information which apply to the analysis of both processes. It has been assumed that there will be joint facilities for storage of carbon tetrachloride at these two-process plants. Total storage control costs are estimated in this chapter, but assessment of the related emissions is divided between this chapter and Chapter 4.

#### 3.1. PERCHLOROETHYLENE CO-PRODUCT PROCESS DESCRIPTION

##### 3.1.1 General Information

Table 3-1 lists names, locations, production capacities, and production processes for the nine carbon tetrachloride production facilities in the U.S. Over half of the total national carbon tetrachloride production capacity is at plants using only the perchloroethylene co-product process (252,000 Mg/yr). An uncertain additional production by the perchloroethylene co-product process is included in the 124,000 Mg/yr total production capacity for plants which also use methane chlorination, but production statistics do not include the division of capacity between the two processes at these plants.

##### 3.1.2 Process Description

At most plants, carbon tetrachloride and perchloroethylene are produced as co-products by high-temperature chlorinolysis of a variety

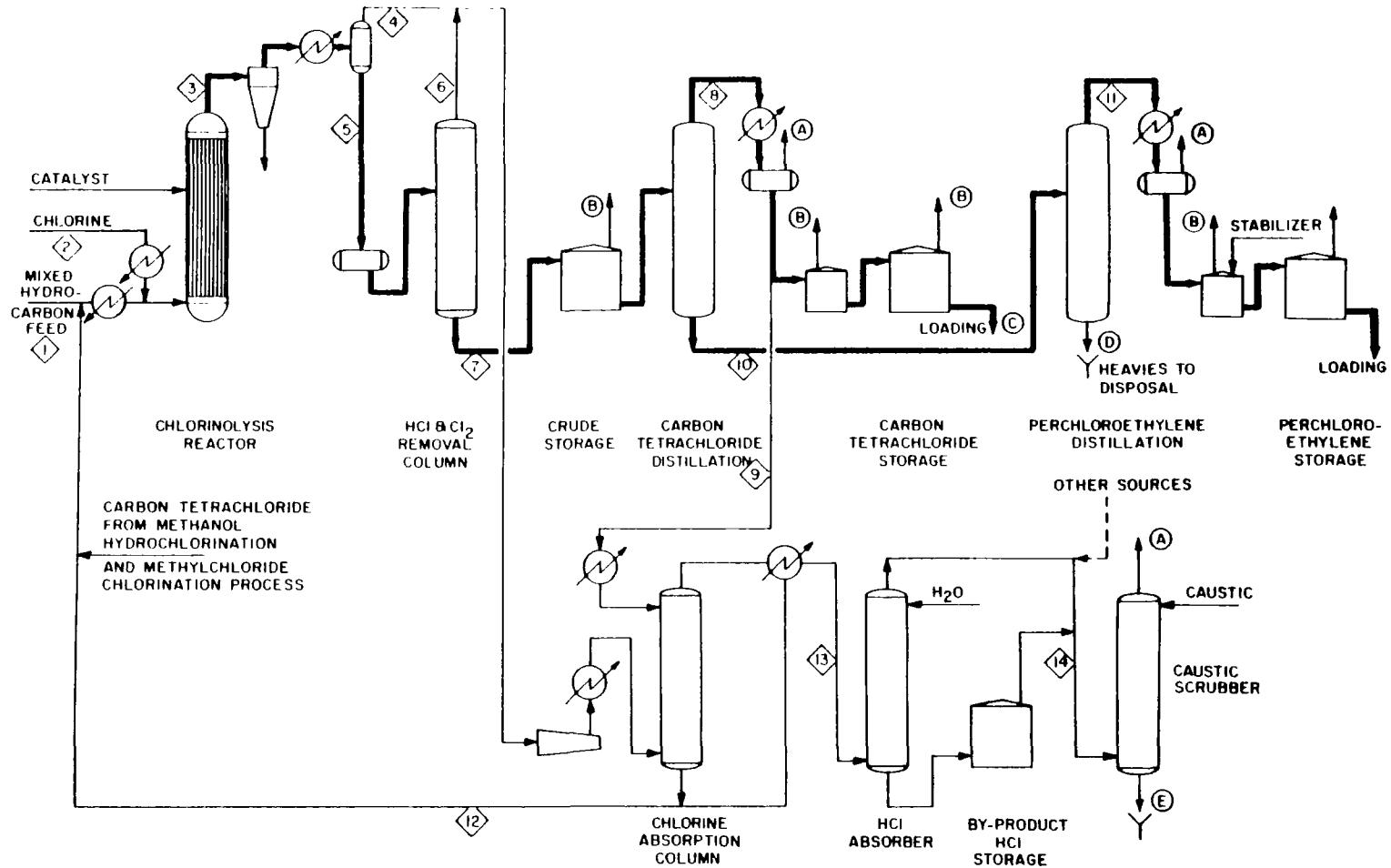
TABLE 3-1. CARBON TETRACHLORIDE PRODUCERS<sup>1</sup>

Plant number	Company	Location	Carbon tetrachloride production capacity (Mg/yr)	Production processes
1	Linden Chlorine	Moundsville, WV	4,000	Methane chlorination
2	Stauffer	LeMoyne, AL	91,000	Carbon disulfide chlorination
3	Stauffer	Louisville, KY	7,000	Methane chlorination
4	Dow	Plaquemine, LA	57,000	Mixed hydrocarbon chlorinolysis with perchloroethylene co-product
5	Vulcan	Geismar, LA	41,000	Mixed hydrocarbon chlorinolysis with perchloroethylene co-product
6	Dow	Freeport, TX	61,000	Methane chlorination and mixed hydrocarbon chlorinolysis with perchloroethylene co-product
7	DuPont	Ingleside, TX	154,000	Methane and ethylene chlorination with perchloroethylene co-product <sup>2,3</sup>
8	Vulcan	Wichita, KS	27,000	Methane chlorination and mixed hydrocarbon chlorinolysis with perchloroethylene co-product
9	Dow	Pittsburg, CA	36,000	Methane chlorination and mixed hydrocarbon chlorinolysis with perchloroethylene co-product
			478,000	

of hydrocarbon feedstocks. Removal and absorption of chlorine and hydrogen chloride and distillation of the two co-products are the other basic process steps. A typical process flow diagram for the perchloroethylene co-product process is shown in Figure 3-1. Feedstocks may include crude carbon tetrachloride, ethylene dichloride, acetylene, ethylene, propylene, napthalene, and paraffinic hydrocarbons of up to four carbons.<sup>5,6</sup> Major feedstocks for each perchloroethylene co-product plant are indicated on Table 3-1. The relative amounts of carbon tetrachloride and perchloroethylene produced are dependent on the feedstock and reaction conditions. The largest plant producing carbon tetrachloride (Plant 7, DuPont at Ingleside, Texas) produces perchloroethylene as a co-product but does not use hydrocarbon chlorinolysis. The process used at the plant is based on chlorination of methane and ethylene feedstocks.<sup>2,3</sup> Since this process is similar to hydrocarbon chlorinolysis, and produces both carbon tetrachloride and perchloroethylene, it has been grouped with hydrocarbon chlorinolysis processes in this report.

### 3.1.3 Carbon Tetrachloride Emission Factors for the Perchloroethylene Co-Product Process

Table 3-2 gives estimated emission factors for the carbon tetrachloride emission points identified in Figure 3-1. Existing emission factors<sup>7,8</sup> were reviewed, resulting in revision of the factor for waste caustic emissions as follows. The IT Enviroscience emission factor for waste caustic (0.15 kg VOC/Mg plant capacity) was based on an average of two emissions which were very different in magnitude and description.<sup>8</sup> One estimate was specific to waste caustic (0.0011 kg VOC/Mg),<sup>3</sup> while the other was for total VOC in plant aqueous waste discharges (0.3 kg VOC/Mg).<sup>9</sup> The original reference indicates that the second figure was actually based on an estimate of total organic carbon in wastewater. Total organic carbon is a parameter used in wastewater engineering which, when properly measured, involves acidification and aeration prior to measurement of organic carbon. Correct procedure will result in loss of volatile organics, including carbon tetrachloride, prior to measurement. This was considered sufficient reason to drop the latter estimate, and the



NOTE: Letters in this figure refer to process vents described in the text and tables. Numbers refer to process descriptions in the first reference cited below. Heavy lines indicate final product streams throughout the process.

Figure 3-1. Process flow diagram for hydrocarbon chlorinolysis process.<sup>4,5</sup>

TABLE 3-2. UNCONTROLLED MODEL PLANT CARBON TETRACHLORIDE EMISSION FACTORS FOR HYDROCARBON CHLORINOLYSIS (PERCHLOROETHYLENE CO-PRODUCT) PROCESS

Emission source	Source designation <sup>a</sup>	Uncontrolled carbon tetrachloride emission factor <sup>b</sup>
Distillation columns	A	0.0058 kg/Mg
Process fugitive <sup>c</sup>		3.2 kg/hr
Storage	B	0.85 kg/Mg
Handling	C	0.24 kg/Mg
Hex waste handling and disposal and waste hydrocarbon storage	D	0.0046 kg/Mg
Waste caustic	E	<0.003 kg/Mg

<sup>a</sup>Source designation shown in Figure 3-1. A is a process component; D and E are secondary emissions.

<sup>b</sup>Emission factors in terms of kg/Mg refer to kg of carbon tetrachloride emitted per Mg of carbon tetrachloride produced. From Reference 7, except Source E, as described in text.

<sup>c</sup>Fugitive emission rate is independent of production rate.

first (0.0011 kg VOC/Mg total plant capacity) was adjusted to reflect the 37.5 percent of total model plant capacity attributed to carbon tetrachloride. The resulting emission factor (0.003 kg VOC/Mg carbon tetrachloride production) was used as an upper bound to potential carbon tetrachloride emissions from waste caustic, because no information was available on the VOC composition.

### 3.2 UNCONTROLLED PERCHLOROETHYLENE CO-PRODUCT PLANT EMISSIONS

A number of preliminary steps were required to allow estimation of uncontrolled carbon tetrachloride emissions from individual production facilities, and also to facilitate later estimates of controlled emissions and control costs for Options 1 and 2. These include use of model plants, apportionment of production capacity to specific production processes, and development of an industry-wide capacity utilization rate. These steps are discussed below, and then uncontrolled emissions for perchloroethylene co-product plants are estimated.

#### 3.2.1 Model Plant

A representative model plant was used as the basis for emission and control cost estimates. The model plant for the perchloroethylene co-product process was chosen to be consistent with those used in previous investigations.<sup>10,11</sup> It was assumed to produce 50,000 Mg/yr of perchloroethylene and 30,000 Mg/yr of carbon tetrachloride. This basic model plant configuration is shown in Figure 3-1. More detail on model plant fugitive emission sources and storage and loading facilities is provided in conjunction with cost estimates in Section 3.5.

It should be noted that use of model plant parameters did not allow consideration of variations between different carbon tetrachloride production facilities. In reality no two processes are the same and several have been reported to vary from the model plants in ways that may affect the accuracy of emission and control cost estimates. Feedstocks, reaction types, purification steps, and in-plant recycle are some of the variables documented by IT Enviroscience.<sup>12</sup> Emission data used in emission factor development were often obtained from single plants and may not apply to all production processes. The relative volume and type

of storage capacity and storage/loading throughputs and associated emissions and costs may vary considerably from the model plant assumptions. For example, proximity to end-use fluorocarbon production facilities will affect the amount of carbon tetrachloride product storage and transportation necessary, since some transfers may be made directly by pipeline.

### 3.2.2 Capacity Apportionment in Two-Process Plants

Plants 6, 8 and 9 (Dow at Freeport, Texas; Vulcan at Wichita, Kansas; and Dow at Pittsburg, California) produce carbon tetrachloride by two processes (methane chlorination and perchloroethylene co-product),<sup>4</sup> but no information is available on the relative contributions of these processes to total carbon tetrachloride production capacities. To derive plant-by-plant emissions and costs from model plant data, it was necessary to apportion the total capacity of these plants to the individual processes. Available total carbon tetrachloride capacities (Table 3-1) were divided between the two processes as follows. Since perchloroethylene production capacities are available for these plants, carbon tetrachloride capacity by the perchloroethylene co-product process was estimated by assuming the proportions of carbon tetrachloride and perchloroethylene co-product capacity from the perchloroethylene co-product process at these plants are the same as that of the model plant (62.5 percent perchloroethylene, 37.5 percent carbon tetrachloride). Remaining carbon tetrachloride capacity was attributed to the methane chlorination process, as shown in Table 3-3.

TABLE 3-3. CAPACITY APPORTIONMENT IN TWO-PROCESS PLANTS (Mg/yr)

Plant	Perchloroethylene Capacity <sup>1</sup>	Carbon Tetrachloride from Perchloroethylene Co-Product Process	Total Carbon Tetrachloride Capacity <sup>1</sup>	Carbon Tetrachloride from Methane Chlorination
6	68,000	40,800	61,000	20,200
8	23,000	13,800	27,000	13,200
9	23,000	13,800	36,000	22,200

### 3.2.3 Proportionality and Scales of Production

Throughout the following analysis, direct proportionality of emissions, control efficiencies and costs over all scales of production was assumed. This approach may introduce significant errors, especially for capital costs, but was considered appropriate due to the lack of detailed technical data and the level of analysis possible in this study. The plant capacity factors in Table 3-4, derived by dividing each plant's assumed carbon tetrachloride production process capacity by that of the perchloroethylene co-product model plant, were used to apply model plant emission estimates and control costs to each plant. Production capacities for two-process plants were estimated in Table 3-3; others were taken directly from Table 3-1.

TABLE 3-4. PERCHLOROETHYLENE CO-PRODUCT PLANT CAPACITY FACTORS (RELATIVE TO MODEL PLANT)

Plant	Plant capacity factor
4	1.9
5	1.36
6	1.36
7	5.13
8	0.46
9	0.46
Total	10.67

### 3.2.4 Capacity Utilization

Based on the 1981 total carbon tetrachloride production of 325,700 Mg,<sup>13</sup> and corresponding national production capacity of 478,000 Mg (Table 3-1), a uniform capacity utilization rate of 0.68 was applied to all carbon tetrachloride plants in estimating uncontrolled and controlled emissions. This factor was used to calculate model plant emission reductions for the cost analyses in Chapters 3, 4 and 5.

### 3.2.5 Uncontrolled Emissions

To estimate uncontrolled emissions for perchloroethylene co-product plants, the uncontrolled full-capacity model plant emissions shown in Table 3-5 were first calculated by multiplying uncontrolled emission factors (Table 3-2) by the 30,000 Mg/yr model plant carbon tetrachloride production capacity. The two secondary emission sources were combined for the purposes of this analysis. The assumed industry-wide capacity utilization factor of 0.68 and the appropriate plant capacity factors from Table 3-4 were then applied to the model plant emission estimates to produce the plant-specific estimates shown in Table 3-6.

TABLE 3-5. PERCHLOROETHYLENE CO-PRODUCT MODEL PLANT EMISSIONS

Source	Model plant carbon tetrachloride emissions (Mg/yr)
Process	0.17
Fugitive	28.0
Storage	25.5
Loading	7.2
Secondary	0.23
Total	61.1

TABLE 3-6. UNCONTROLLED EMISSIONS FOR PERCHLOROETHYLENE CO-PRODUCT PLANTS

Plant number	Uncontrolled emission estimates (Mg/yr)					
	Process	Fugitive	Storage	Loading	Secondary	Total
4	0.21	36.2	33.0	9.3	0.30	79.0
5	0.16	25.9	23.6	6.7	0.21	56.5
6	0.16	25.9	23.6	6.7	0.21	56.5
7	0.59	97.6	88.9	25.1	0.80	213.0
8	0.05	8.8	8.0	2.2	0.07	19.0
9	0.05	8.8	8.0	2.2	0.07	19.0
Total	1.22	203.2	185.1	52.2	1.66	443.0

### 3.3 OPTION 1 CONTROLS AND EMISSIONS FOR PERCHLOROETHYLENE CO-PRODUCT PLANTS

Option 1 control efficiencies represent the most stringent of existing, State-required or applicable Group III CTG controls for areas requesting an ozone NAAQS attainment date extension beyond 1982. These controls are discussed individually below as they apply to perchloroethylene co-product plants. They are then combined to define Option 1 control efficiencies for each source category at each plant, and used to estimate controlled emissions under Option 1. Since State regulations and the Group III CTGs and their assumed control efficiencies are discussed in detail in Section 2.2, their discussion here is limited to their applicability to given plants and other plant-specific considerations. For ease of reference, the tables presented in this section include existing controls and State regulations for all carbon tetrachloride production facilities, including the methane chlorination and carbon disulfide process plants discussed in Chapters 4 and 5.

#### 3.3.1 Existing Controls

Information on control technology currently in place at carbon tetrachloride production facilities was obtained mainly in telephone conversations with State agency personnel. Some data were available from previous EPA industry surveys. Table 3-7 summarizes the information on existing controls. Control efficiencies were provided either in the cited references, or derived from technical data in them. In most cases, unreported efficiencies were estimated to be proportional to vapor pressure reductions achieved by given condenser outlet temperatures. Since all carbon tetrachloride plants are believed to have emissions in all major emission categories (process, fugitive, storage, handling, secondary), Table 3-7 shows that most emission points at most carbon tetrachloride plants are not controlled. In addition, some of the controls listed in Table 3-7 do not cover all emission points in the applicable emission category, so the listed control efficiency does not apply to the entire emission category. For perchloroethylene co-product plants, these include the secondary emission controls at Plants 6 and 7, which each apply to only one of the two components of secondary emissions

TABLE 3-7. KNOWN EXISTING CONTROLS AT CARBON TETRACHLORIDE PRODUCTION PLANTS

Plant number	Emission category	Control device	Control efficiency (%)	Reference
1	Process <sup>a</sup>	Process vent condensation system.	50	14
2	Process	Two-stage refrigerated condenser on chlorination reactor; 120 lb/hr controlled emissions	95	15
3	Storage	Brine-cooled condenser on a 2,400 gallon fixed-roof carbon tetrachloride storage tank and several tanks for other products.	50	16
4	Storage	Vapor recovery (-20°C refrigerated condenser) on single large fixed-roof carbon tetrachloride tank (five small tanks with no control).	95	17
5	Process	Refrigerated condenser on carbon tetrachloride/perchloroethylene process tower.	90	14, 17
	Storage	Vapor recovery (-7°C refrigerated condensers) on 160,000 and 6,000,000 gallon fixed-roof storage tanks (four 8,000 gallon product check tanks and a 13,000 gallon re-run tank with no controls).	80	17, 18
6	Storage	Refrigerated condensers and pressurized-nitrogen padding on fixed-roof tanks.	95	14, 19
	Secondary <sup>a</sup>	Vapor-balance, refrigerated condensation and recycle used on hex waste handling and feed storage tanks for perchloroethylene co-product process.	99	20

CONTINUED

TABLE 3-7. (continued)

Plant number	Emission category	Control device	Control efficiency (%)	Reference
7	Secondary <sup>a</sup>	Waste caustic from organic neutralization system is steam-stripped of VOC, which is recycled to the process.	96	20
8		No controls exist.	0	21
9		No controls exist.	0	22

<sup>a</sup>Controls only part of this emission category -- see text for details.

from this process (waste caustic; hex waste handling and disposal, and waste hydrocarbon storage). It was necessary to use the original emission factors for these components (Table 3-2) and the available control efficiencies (Table 3-7) to estimate overall secondary emission control of these plants. Thus, 96 percent control of waste caustic emissions, which comprise about 40 percent of secondary emissions, results in about 40 percent control of total secondary emissions at Plant 7. Similarly, 99 percent control of hex waste handling and disposal and waste hydrocarbon storage at Plant 6 will provide about 60 percent of total secondary emissions. The carbon tetrachloride control efficiencies for the larger storage tanks at Plants 4 and 5 were applied to total storage emissions. Implicit in this is the assumption that the smaller tanks have negligible emissions, due to their size, the lower carbon tetrachloride content of crude product, and relatively constant operating levels.<sup>23</sup>

### 3.3.2 State Regulations

Current State regulations applying to carbon tetrachloride production facilities and related efficiencies were extracted from Section 2.2 and are summarized in Table 3-8.

Carbon tetrachloride is not covered by the definition of "VOC" applicable to VOC storage and fugitive VOC in Louisiana, or by the definition of "organic liquid" which applies to VOC storage in the San Francisco Bay Area (California). (See 2.2.1 for the full definitions.) For purposes of this source assessment, however, it has been assumed that the Louisiana and Bay Area SIP provisions cited for Plants 4, 5 and 9 in Table 3-8 will be enforceable for carbon tetrachloride despite the current State definitions. This assumption does not appear unreasonable for Option 1, since the Bay Area definition will probably be changed to conform with the VOC definition in the VOL storage CTG when this CTG is adopted there, and since Louisiana is currently applying its VOC regulations to carbon tetrachloride sources.<sup>17</sup>

Unless otherwise indicated, it is assumed that the plants are subject to the regulations and control requirements cited in Table 3-8.

TABLE 3-8. CURRENT STATE REGULATIONS APPLYING TO CARBON TETRACHLORIDE PRODUCTION FACILITIES

Plant number	State	Applicable State regulations <sup>a</sup>	Control efficiency (%) <sup>a</sup>
1	West Virginia	None.	--
2	Alabama (Mobile Co.)	<u>VOC Storage:</u> Tanks over 1,000 gallons must be pressure tanks or have either (a) submerged fill, (b) external or internal floating roof, (c) vapor recovery system, or (d) other equipment or means of equal efficiency.	0
		<u>VOC Loading:</u> Loading of tanks, trucks, or trailers must employ (a) either vapor collection and disposal or a system allowing 95 percent submerged fill or equivalent, (b) prevention of liquid drainage from the loading device, and (c) vapor-tight and automatic-closing loading line connectors, unless hatch-loaded.	0
3	Kentucky	None (regulations only cover petroleum liquids and/or gasoline).	--
4,5	Louisiana	<u>VOC Storage:</u> Tanks over 40,000 gallons which are not pressure tanks must have submerged fill and either (a) floating roof, (b) a vapor loss control system equivalent to floating roof, or (c) other equivalent equipment or means. Tanks from 250 to 40,000 must have submerged fill or vapor recovery or other equivalent equipment or means.	95
		<u>VOC Loading:</u> Facilities with daily throughput of 40,000 gallons or more must have vapor recovery and disposal, or an equivalent, and spill	90

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CONTINUED

TABLE 3-8. (continued)

Plant number	State	Applicable State regulations <sup>a</sup>	Control efficiency (%) <sup>a</sup>
4,5 (continued)		prevention for filling equipment. (Plant 4 is exempt, as described in the text.)	
		<u>VOC Fugitives:</u> Pumps and compressors must be equipped with mechanical seals, or equivalent equipment or means. Best practical housekeeping and maintenance practices are also required.	0
		<u>Process:</u> Louisiana's requirement for waste gas combustion or equivalent control does not apply to non-combustible gases or sources under 100 tons (91 Mg) per year, exempting Plants 4 and 5.	NA
3-15 6	Texas (Brazoria Co.)	<u>VOC Storage:</u> Tanks from 1,000 to 25,000 gallons must have submerged fill. Tanks from 25,000 to 42,000 gallons must have any type of floating roof or a vapor recovery system which reduces vent gas vapor pressure to 1.5 psia. Tanks over 42,000 gallons must have an internal floating roof, an external floating roof with vapor-mounted primary seal and secondary seal, or a vapor recovery system which reduces vapor pressure to 1.5 psia.	50
		<u>VOC Loading:</u> Facilities with average throughputs over 20,000 gallons per day must have a vapor recovery system which reduces the true vapor pressure of vent gases to 1.5 psia, vapor-tight seal, and drainage control (ship and barge loading exempt).	50
		<u>Process:</u> Texas regulations do not apply to carbon tetrachloride.	NA

CONTINUED

TABLE 3-8. (continued)

Plant number	State	Applicable State regulations <sup>a</sup>	Control efficiency (%) <sup>a</sup>
7	Texas (San Patricio Co.)	<u>VOC Storage:</u> Tanks over 1,000 gallons must have submerged fill or vapor recovery if not a pressure tank. Tanks over 25,000 gallons must be pressure tanks or have either a floating roof or a vapor recovery system reducing vent gas vapor pressures to 1.5 psia.  <u>VOC Loading:</u> Facilities with average throughputs of 20,000 gallons per day must have a vapor recovery system reducing vent gas vapor pressures to 1.5 psia, vapor-tight seal, and drainage control (ship and barge loading exempt).	50
8	Kansas	<u>Process:</u> Texas regulations do not apply to carbon tetrachloride.	NA
9	California (Bay Area)	<u>Valves and Flanges:</u> Annual inspection and repair or minimization of leaks is required in chemical plant complexes.  <u>VOC Storage:</u> Organic liquid storage tanks between 260 and 40,000 gallons must have submerged fill or equivalent. Tanks over 40,000 gallons must have floating roof, vapor recovery with 95 percent efficiency or other control with 95 percent efficiency.	0
			95

<sup>a</sup>See Section 2.2 for references and discussion of control efficiency estimates. 0 indicates requirements which have no effect since they are equivalent to the uncontrolled case; NA indicates controls not required due to size cutoff or other exemption, as discussed in the text.

Exemptions have been identified in the following cases. Plant 4 (Dow/Plaquemine) has been exempted from loading controls by the Louisiana Air Quality Division, having demonstrated daily throughput of less than 40,000 gallons for the facility handling carbon tetrachloride. Plant 5 (Vulcan/Geismar) is not exempt, due to loading of other products in excess of 40,000 gallons per day. Process vent emissions at Plants 4 and 5 are also assumed to be exempt from Louisiana's regulations, since calculations of their uncontrolled emissions in this study and information available from the Louisiana Air Quality Division indicate total process VOC emissions are well under 100 tons per year. According to the original source of the data used in the 0.0058 kg/Mg uncontrolled emission factor for perchloroethylene co-product process distillation columns, carbon tetrachloride is the only VOC emitted at this point.<sup>3</sup> Thus the 0.21 and 0.16 Mg/yr uncontrolled process emissions for Plants 4 and 5 (Table 3-6) represent total VOC, and are well under 100 tons per year. Contacts at the State agency indicate that both plants have actually been exempted from process control, due to low emission levels. Vulcan reports process VOC emissions of 1.2 tons per year, based on tests of the carbon tetrachloride tower reflux drum, and total Dow process VOC emissions are also believed to be less than 5 tons per year.<sup>24</sup> It is assumed that Texas process control regulations do not apply to process vent emissions at perchloroethylene co-product plants, because carbon tetrachloride is not on the list of affected compounds, and, as described above, is believed to be the only VOC in this vent stream. Plants 6 and 7 are assumed to be covered by the Texas regulations for VOC loading, since the annual carbon tetrachloride production capacity for the smaller Plant 6 (61,000 Mg/yr) would result in an average daily loading rate of over 27,000 gallons. The Texas regulations' exemption limit is 20,000 gallons per day. Loading of perchloroethylene and other products would increase the average throughput for these loading facilities by at least a factor of two, so it was assumed that these plants would exceed the exemption limit even with substantial barge and ship loading.

### 3.3.3 Group III Control Techniques Guidelines

Table 3-9 summarizes the current status of counties with carbon tetrachloride production facilities with respect to the National Ambient Air Quality Standard for ozone. Since it is anticipated that ozone nonattainment areas which have received extensions beyond 1982 will be required to adopt all Group III CTGs, it has been assumed that the CTGs discussed in 2.2.2 apply to the Dow perchloroethylene co-product plant at Pittsburg, California (Plant 9), and will result in 42 percent control of fugitive emissions and 95 percent control of storage emissions. Plant 3 (Stauffer/Louisville, KY) is also subject to these requirements, but is addressed in Chapter 4 with the methane chlorination process plants.

TABLE 3-9. OZONE NATIONAL AMBIENT AIR QUALITY STANDARD ATTAINMENT STATUS FOR CARBON TETRACHLORIDE PRODUCTION FACILITIES<sup>25,26</sup>

Plant number	Ozone NAAQS attainment status	Post-1982 attainment date granted?
1	Attainment	--
2	Nonattainment	No
3	Nonattainment	Yes
4	Nonattainment	No
5	Nonattainment	No
6	Nonattainment	No
7	Attainment	--
8	Attainment	--
9	Nonattainment	Yes

### 3.3.4 Combined Option 1 Controls

Table 3-10 summarizes control efficiencies applicable to perchloroethylene co-product plants for the Option 1 controls described in 3.3.1, 3.3.2, and 3.3.3. Each efficiency represents the most stringent of existing, State-required or Group III CTG controls. Table 3-11 provides more detail on the estimated efficiencies of these three control categories with respect to storage emissions. The most stringent level of control for each plant was selected as the Option 1 storage control shown in Table 3-10.

TABLE 3-10. OPTION 1 CONTROL SUMMARY FOR PERCHLOROETHYLENE CO-PRODUCT PLANTS

Plant	Process	Option 1 control efficiency (percent)			
		Fugitive	Storage	Loading	Secondary
4	--	--	95	--	--
5	90	--	95	90	--
6	--	--	95	50	60
7	--	--	50	50	40
8	--	--	--	--	--
9	--	42	95	--	--

TABLE 3-11. OPTION 1 CONTROLS FOR STORAGE EMISSIONS AT PERCHLOROETHYLENE CO-PRODUCT PLANTS

Plant	Existing control	Current regulations	Group III CTG
4	95	95	--
5	80	95	--
6	95	50	--
7	--	50	--
8	--	--	--
9	--	95	95

### 3.3.5 Estimated Option 1 Emissions

Applying the control efficiencies in Table 3-10 to uncontrolled emission estimates (Table 3-6) produced the Option 1 controlled emission estimates in Table 3-12.

TABLE 3-12. OPTION 1 CONTROLLED EMISSIONS FOR PERCHLOROETHYLENE CO-PRODUCT PLANTS

Plant	Process	Option 1 controlled emissions (Mg/yr)				Total
		Fugitive	Storage	Loading	Secondary	
4	0.21	36.2	1.7	9.3	0.30	47.7
5	0.02	25.9	1.2	0.7	0.21	28.0
6	0.16	25.9	1.2	3.4	0.08	30.7
7	0.59	97.6	44.5	12.6	0.48	155.8
8	0.05	8.8	8.0	2.2	0.07	19.1
9	0.05	5.1	0.4	2.2	0.07	7.8
Total	1.08	199.5	57.0	30.4	1.21	289.2
Option 1 control efficiency (%)	11	2	69	42	27	35

### 3.4 OPTION 2 CONTROLS AND EMISSIONS FOR PERCHLOROETHYLENE CO-PRODUCT PLANTS

This section describes the estimated best controls (EBC) used in Option 2, and estimates the emissions expected after application of these controls to perchloroethylene co-product plants.

#### 3.4.1 Estimated Best Controls

The following control methods were selected as EBC for carbon tetrachloride plants using the perchloroethylene co-product process. All control efficiencies cited are specific to carbon tetrachloride.

Process emissions: Refrigerated condensers have been reported to provide 90 percent control of carbon tetrachloride/perchloroethylene distillation columns.<sup>14</sup>

Fugitive emissions: An inspection and repair program similar to the Group III CTG can provide 42 percent control,<sup>27</sup> but EBC include addition of equipment specifications estimated to raise this to about 56 percent.<sup>28</sup>

Storage emissions: Vapor recovery and -20°C refrigerated condensation systems can be used to control carbon tetrachloride storage at efficiencies up to 95 percent.<sup>14,19,29</sup>

Loading emissions: Vapor recovery, refrigerated condensers and tank truck leakage reduction measures are estimated to provide 90 percent control of loading emissions.<sup>30,31</sup>

Secondary emissions: Combined use of steam-stripping of waste caustic and vapor balance, condensation and recycle for hex waste and waste hydrocarbon storage can provide 98 percent control of secondary emissions from carbon tetrachloride/perchloroethylene processes.<sup>20</sup>

### 3.4.2 Estimated Option 2 Emissions

Table 3-13 summarizes annual emissions and control efficiencies which can be achieved by perchloroethylene co-product plants with the Option 2 controls described in 3.4.1.

TABLE 3-13. OPTION 2 CONTROLLED EMISSIONS FOR PERCHLOROETHYLENE CO-PRODUCT PLANTS

Plant	Process	Option 2 controlled emissions (Mg/yr)					Total
		Fugitive	Storage	Loading	Secondary		
4	0.02	15.9	1.7	0.9	0.006	18.5	
5	0.02	11.4	1.2	0.7	0.004	13.3	
6	0.02	11.4	1.2	0.7	0.004	13.3	
7	0.06	42.9	4.4	2.5	0.016	49.9	
8	0.01	3.9	0.4	0.2	0.001	4.5	
9	0.01	3.9	0.4	0.2	0.001	4.5	
Total	0.14	89.4	9.3	5.2	0.032	104.0	
Option 2 control efficiency (%)	90	56	95	90	98	77	

### 3.5 CONTROL COSTS FOR PERCHLOROETHYLENE CO-PRODUCT PLANTS

This section presents control cost estimates for the Option 1 and Option 2 controls discussed in this chapter. Model plant costs are developed for each source type (process, storage, etc.) and plant-specific costs for Options 1 and 2 are presented under Summary headings at the end of 3.5.1 and 3.5.2. In a few cases, the model plant approach could not be used, and full control costs for individual plants are developed. Costing methodology and assumptions are discussed further in Chapter 1. All costs are for July 1982 except where noted. Examples and details of control requirement calculations are presented in Appendix B.

#### 3.5.1 Option 1 Control Costs

This section provides cost estimates for the Option 1 perchloroethylene co-product plant controls discussed in 3.3.4.

Process controls: Plant 5 is the only perchloroethylene co-product plant with Option 1 process control, a refrigerated condenser reported to provide 90 percent control.<sup>14,17</sup> Since the same control is used for all other perchloroethylene co-product plants under Option 2, applicability of the following cost estimate to these plants is also described.

As discussed below, the gas flowrates and refrigeration requirements for documented perchloroethylene co-product process vent streams are more than two orders of magnitude below the operating levels of standard condensing units for which costs are available.<sup>32-35</sup> The emissions in question actually come from in-process condensers in distillation systems. The control efficiency cited for Plant 5 may represent upgrading of the in-process condenser or installation of a two-stage condenser system rather than use of a separate add-on condenser. The type of control actually in use could not be verified. Since available process data would not allow assessment of these possibilities, this control device was assumed to be a retrofit condenser under Options 1 and 2. Technical data from two perchloroethylene co-product plants were used to specify flow rate and refrigeration capacity for a small retrofit refrigerated condenser, as described in Appendix B-1.

The refrigeration requirement of 22 BTU/hr and flowrates under 0.1 ft<sup>3</sup>/min derived in Appendix B-1 reflect the small flow and emission rates for these process vents. These specifications are far below the smallest streams for which standardized cost estimates have been developed (100 ft<sup>3</sup>/min)<sup>35</sup>, and are considerably smaller than the capacity of the smallest applicable standard unit available from a major manufacturer of condensation equipment, which has a cooling capacity of 3,600 BTU/hr.<sup>34</sup> This 3,600 BTU/hr unit would have a base capital cost of about \$3,500 and has an outlet brine temperature of -25°C. The cost of a smaller unit is very difficult to estimate, due to the need for custom engineering, and procurement and fabrication of non-standard parts. It was assumed that \$3,500 is a reasonable upper-bound estimate of the base capital cost of a refrigerated condenser for 90 percent control of process emissions at perchloroethylene co-product plants, because the specifications above were developed for Plant 7, the largest plant of this type. In most other cost estimates, direct proportionality of control costs to plant size has been assumed. In this case, however, such an approach would not be appropriate because smaller condensers do not exist. For this reason, the \$3,500 base capital cost was used directly and a model plant-based costing approach was not used.

Allowing 18 percent of the base cost for taxes, freight, and instrumentation and 61 percent for installation,<sup>36</sup> total installed capital cost would be \$6,650. A 29 percent annualized cost factor, including maintenance labor and material (6 percent), taxes, insurance and administration (5 percent), and capital recovery (18 percent), developed specifically for condensers,<sup>37</sup> results in an annualized capital cost of \$1,930 for each plant. IT Enviroscience estimates electric utility costs in the range of 2 to 6 percent of annualized capital cost for 95 percent control of a 20 percent VOL stream.<sup>38</sup> Assuming 5 percent results in an estimated annual utility cost of about \$100 for the model plant. The manufacturer reports that such small, simple units will have minimal operating labor requirements, possibly 10 minutes per week.<sup>34</sup> On an annual basis, at \$19/hour,<sup>37</sup> this results in an annual labor cost of about \$165.

An Option 1 emission reduction of 0.14 Mg/yr (from Tables 3-6 and 3-12) results in the following net Option 1 process control cost and cost-effectiveness for Plant 5.

Total installed capital cost	<u>\$6,650</u>
Annualized capital cost	\$1,930
Utilities and labor	<u>\$ 265</u>
Total annualized cost for Option 1 (Plant 5)	\$2,195
Recovery credit	<u>(59)</u>
Net annualized cost	\$2,136
Emission reduction	0.14 Mg/yr; 90%
Cost-effectiveness	\$15,300/Mg

Fugitive control: The following procedure was used to estimate costs of Option 1 fugitive emission controls at Plant 9. Based on the model plant fugitive emission source inventory and process descriptions from IT Enviroscience,<sup>39</sup> estimates of the number of fugitive sources in carbon tetrachloride service at perchloroethylene co-product plants were made (Table 3-14). Comparing the carbon tetrachloride sources which would be included in a fugitive emission control program to those used in the small model plant in the SOCMI fugitives CTG, it was assumed that use of control costs for this small SOCMI model plant would result in a reasonable estimate of the likely control costs for the Option 1 inspection and maintenance program for the carbon tetrachloride/perchloroethylene co-product model plant. The small SOCMI model plant is estimated to have a capital cost of control of \$19,200 and an annualized cost of \$14,200 for quarterly monitoring, maintenance, and associated administration, a program estimated to result in 42 percent control.<sup>27</sup> Combined with applicable model plant emission reductions at 0.68 capacity utilization, net costs and cost-effectiveness for the model plant are estimated below. These model plant costs were combined with the Plant 9 capacity factor (Table 3-4) to arrive at the the estimated Plant 9 costs in Table 3-21.

TABLE 3-14. MODEL PLANT FUGITIVE EMISSION SOURCES

	Perchloroethylene co-product model plant		Small SOCMF fugitives model plant <sup>40</sup>
	Total fugitive sources <sup>39</sup>	In carbon tetrachloride service	
Pumps	30	10	15
Process valves	800	280	230
Relief valves	12	4	12
Compressor	1	0	1
Total installed capital cost		\$19,200	
Annualized cost		\$14,200	
Recovery credit for carbon tetrachloride		(3,343)	
Net annualized cost		\$10,857	
Emission reduction		8.0 Mg/yr; 42%	
Cost-effectiveness		\$1,357/Mg (cost)	

Storage controls: This discussion addresses the general assumptions and cost estimates which apply to both perchloroethylene co-product and methane chlorination model plants. These costs will then be used to estimate Option 1 perchloroethylene co-product model plant storage control costs, which apply to Plants 4, 5 and 7. These basic costs will also be used to estimate Option 1 storage control costs at Plants 6 and 9, which use both production processes, assuming joint product storage at these plants. Storage control costs for the two major carbon tetrachloride production processes are based on model plant storage parameters and available cost data for similar control scenarios previously developed by IT Enviroscience. Storage facilities for the model plants are shown in Tables 3-15 and 3-16.

TABLE 3-15. PERCHLOROETHYLENE CO-PRODUCT MODEL PLANT STORAGE<sup>41</sup>

	Number of tanks	Size (m <sup>3</sup> )	Turnovers per year	Temperature (°C)
Crude product	1	378	6	38
Carbon tetrachloride	2	76	125	35
Carbon tetrachloride	1	757	25	20

TABLE 3-16. METHANE CHLORINATION MODEL PLANT STORAGE<sup>42</sup>

	Number of tanks	Size (m <sup>3</sup> )	Turnovers per year	Temperature (°C)
Crude product	1	757	6	35
Carbon tetrachloride	2	38	166	35
Carbon tetrachloride	1	757	17	20

Costs for refrigerated condensers on VOC storage tanks were available in Volume 3 of the IT Enviroscience SOCMI study.<sup>43</sup> It was assumed that costs for condenser control of storage emissions at either of the above model plants could be derived from the costs for condenser control of the IT Enviroscience model storage tank which has a capacity of 660 m<sup>3</sup> and 50 turnovers per year. This assumption is based on a number of simplifying assumptions: (1) a single condensation system can be used for all tanks;<sup>44</sup> (2) working losses for the crude product tanks are small due to relatively constant operating levels;<sup>45</sup> (3) condenser size and cost are most dependent on the maximum rate of working losses,<sup>44</sup> which would be from the large carbon tetrachloride storage tank for each model plant; and (4) working losses for the large model plant storage tanks (757 m<sup>3</sup>, 17-25 turnovers per year) plus those for the two smaller model plant product storage tanks will be roughly equivalent to working losses from the IT Enviroscience model tank, which is somewhat smaller than the large tank but has a

higher turnover rate. Annualized costs and control efficiencies for two control scenarios for the cited IT Enviroscience model tank (Case 2, Case 3) were used to draw Figure 3-2. Case 1 was not used because the VOC for that scenario was not sufficiently similar to carbon tetrachloride. Allowance was made for the higher vapor pressure of the VOC in Case 3. The annualized control costs for Option 1 and 2 control levels in Table 3-17 were estimated using Figure 3-2, and inflated to July 1982. Since the Enviroscience cost estimates neglected utility and operating labor costs, it was possible to derive the estimated capital costs in Table 3-17 from the respective annualized costs with the total Enviroscience annualized cost factor (0.29). This factor includes maintenance, capital recovery and miscellaneous capital-related costs.<sup>46</sup>

TABLE 3-17. ESTIMATED MODEL PLANT COSTS FOR REFRIGERATED CONDENSER STORAGE CONTROL (PERCHLOROETHYLENE CO-PRODUCT AND METHANE CHLORINATION)

Control efficiency (percent)	Capital cost of complete condenser system	Annualized cost of complete condenser system
95	\$285,000	\$82,600
50	26,300	7,600

Applying the above cost estimates to storage control efficiencies relevant to Option 1 for perchloroethylene co-product plants and model plant emissions data produces the following net annualized cost and cost-effectiveness data for the perchloroethylene co-product model plant. These costs and plant capacity factors (Table 3-4) are the basis for the storage control costs for Plants 4 and 5 (95 percent control) and Plant 7 (50 percent control). These plant-specific costs are shown in Table 3-21.

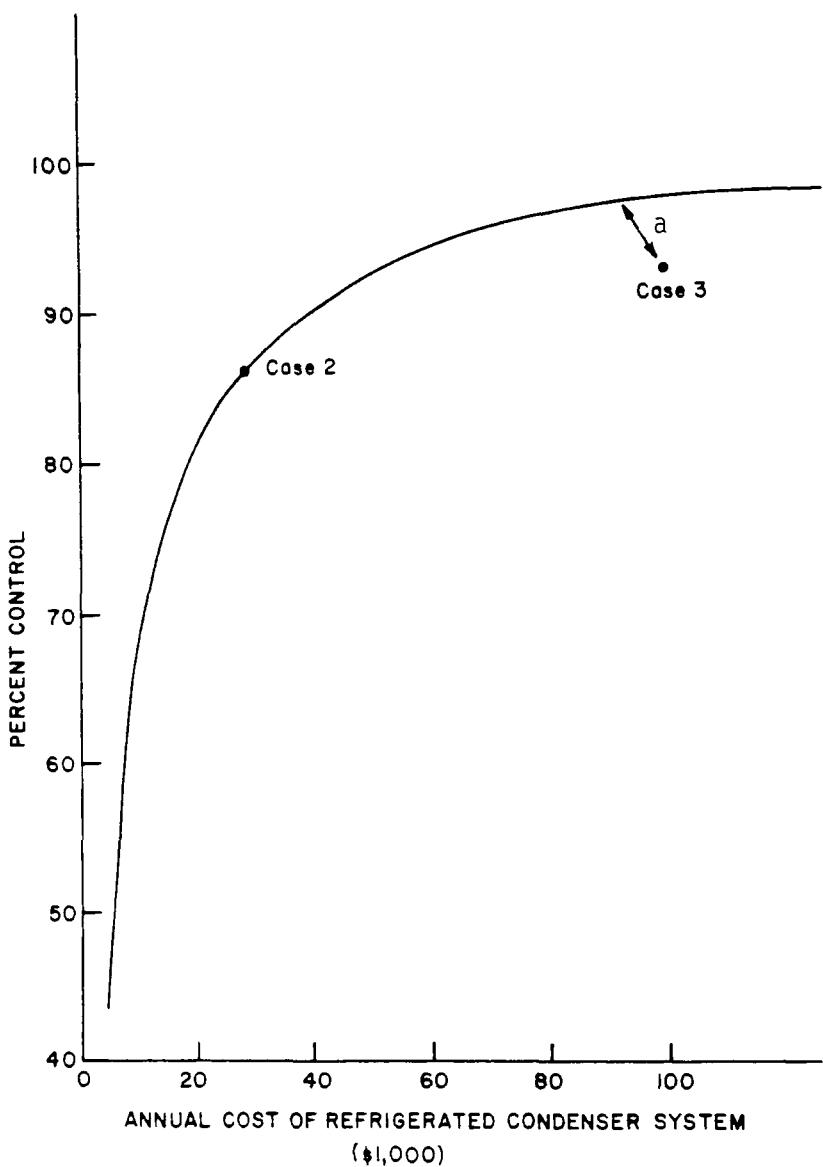


Figure 3-2. Estimated annual costs of condensers for carbon tetrachloride storage in December 1979 (660 m<sup>3</sup> tank with 20 turnovers per year).<sup>43</sup>

<sup>a</sup>Some allowance was made for the higher vapor pressure VOC used in Case 3. The Case 2 VOC was very similar to carbon tetrachloride. Due to the difference between carbon tetrachloride and the VOC assumed, Case 1 was not considered.

	<u>95 percent control</u>	<u>50 percent control</u>
Total installed capital cost	<u>\$285,000</u>	<u>\$26,300</u>
Annualized cost	82,600	7,600
Recovery credit	(6,900)	(3,600)
Net annualized cost	<u>\$ 75,700</u>	<u>\$ 4,000</u>
Emission reduction	16.5 Mg/yr	8.7 Mg/yr
Cost-effectiveness	\$4,600/Mg	\$460/Mg

Option 1 storage controls at two-process plants consist of 95 percent control at Plants 6 and 9. The \$285,000 capital cost and \$82,600 annualized control cost for the model plants (Table 3-17) were scaled to the size of Plants 6 and 9 using their combined plant capacity factors from Tables 3-4 and 4-2. This resulted in overall plant capacity factors of 2.37 for Plant 6 and 1.57 for Plant 9. To estimate net annualized cost and cost-effectiveness, it was necessary to calculate the two Option 1 emission reductions for each plant from Tables 3-6, 3-12, 4-4 and 4-7.

	<u>Plant 6</u>	<u>Plant 9</u>
Total installed capital cost	<u>\$675,500</u>	<u>\$447,500</u>
Annualized cost	195,900	129,700
Recovery credit	( <u>12,700</u> )	<u>(6,700)</u>
Net annualized cost	183,200	123,000
Emission reduction	30.3 Mg/yr 95%	16.1 Mg/yr 95%
Cost-effectiveness	\$ 6,050/Mg	\$ 7,640/Mg

Loading Controls: The best available costs for loading controls are from the December 1980 Draft EIS for the Bulk Gasoline Terminals NSPS.<sup>47</sup> To use this information, a number of assumptions were necessary. Gasoline

terminals for which costs were available ranged in throughput from 380 to 3800 m<sup>3</sup> per day, while average carbon tetrachloride model plant throughputs are 34 m<sup>3</sup>/day for methane chlorination and 52 m<sup>3</sup>/day for the perchloroethylene co-product process. Extrapolation down to these ranges introduces considerable uncertainty into the costs assumed for carbon tetrachloride plants. Due to this uncertainty, additional errors introduced by applying costs of condenser systems designed for control of gasoline vapors to carbon tetrachloride loading facilities and the use of nearly-identical retrofit and new-plant control costs in the NSPS are considered minor. It was also necessary to assume that control costs thus derived from bottom-loaded gasoline loading facilities would be appropriate to carbon tetrachloride loading, despite possible differences in equipment, location, and other factors. It was assumed that the control systems costed in the NSPS could attain a 90 percent control efficiency.<sup>48</sup>

Table 3-18 presents annualized costs for refrigerated condensers at gasoline bulk terminals from which normalized costs per cubic meter of throughput were derived. These normalized costs were used to draw the curve in Figure 3-3, which extrapolates loading control costs for gasoline terminals (points A through D) to the throughput range of the carbon tetrachloride model plants. Points 1, 2 and 3 on Figure 3-3 represent normalized annualized costs for 90 percent control of loading emissions at the carbon tetrachloride model plant throughputs. From the calculations on Figure 3-3, the normalized annualized control cost converts to a July 1982 cost of \$31,300/yr for the perchloroethylene co-product model plant. A corresponding capital cost of \$101,700 was estimated by (1) assuming capital charges to be about 65 percent of the total annualized cost (the plants in Table 3-18 range from 64 percent for the smallest to 61 percent for the largest), and (2) applying the 0.20 annualized cost factor used to derive capital charges in the original reference.<sup>49</sup> These costs result in the following net cost and cost-effectiveness figures, based on 90 percent reduction of model plant loading emissions (Table 3-5), and 0.68 capacity utilization.

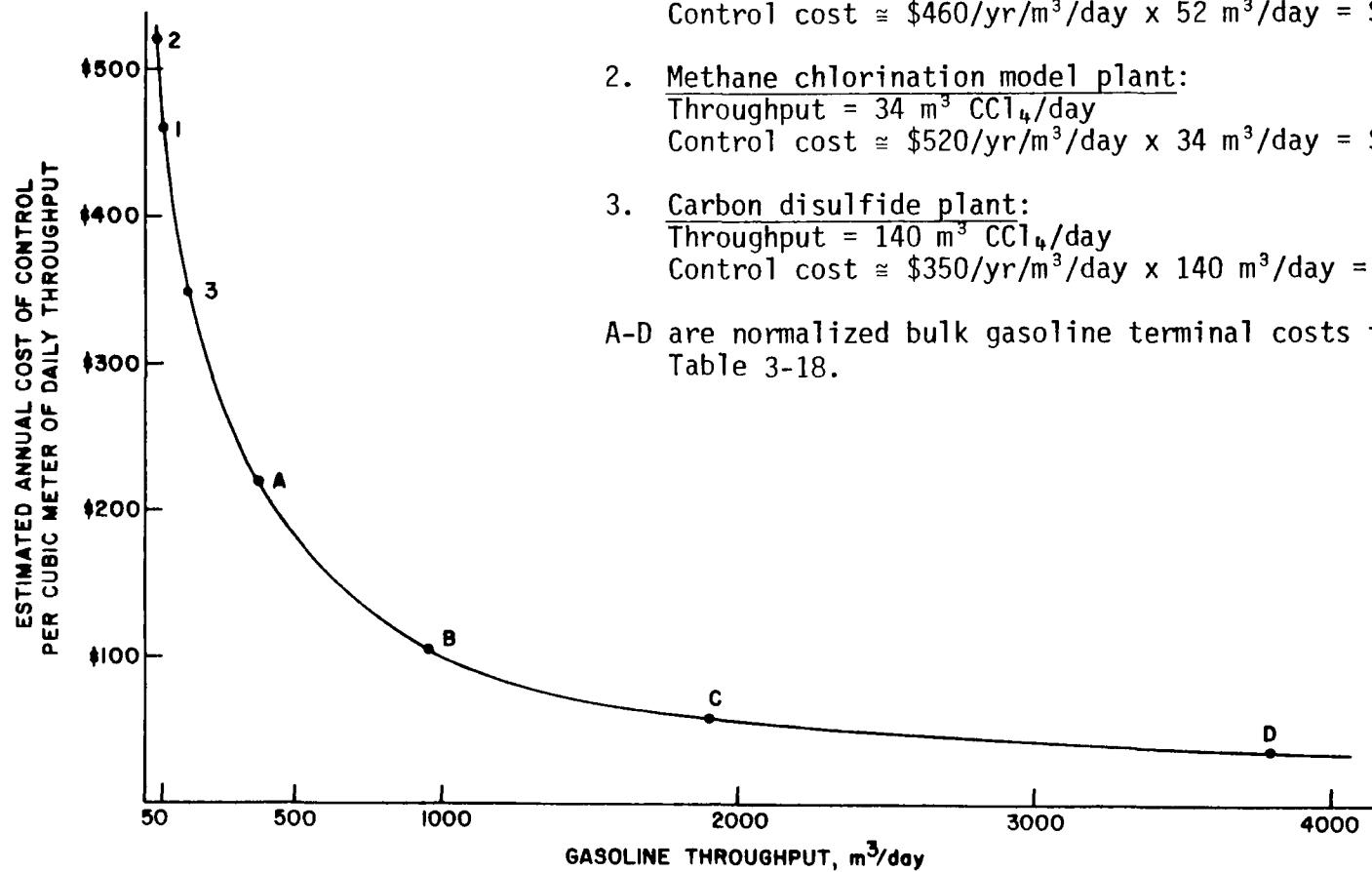


Figure 3-3. Bulk Gasoline Terminals NSPS control costs (mid-1979).<sup>47</sup>

Total installed capital cost	<u>\$101,700</u>
Annualized cost	31,300
Recovery credit	<u>(1,840)</u>
Net annualized cost	29,460
Emission reduction	4.4 Mg/yr; 90%
Cost-effectiveness	\$ 6,700/Mg

TABLE 3-18. ANNUALIZED REFRIGERATED CONDENSER CONTROL COSTS FOR EXISTING BOTTOM-LOADED BULK GASOLINE TERMINALS<sup>47</sup>  
(\$1,000, mid-1979)

NSPS costs	Throughput			
	380 m <sup>3</sup> /day	950 m <sup>3</sup> /day	1,900 m <sup>3</sup> /day	3,300 m <sup>3</sup> /day
Direct operating costs	30.1	38.1	41.0	54.6
Truck maintenance	0.5	0.9	1.4	3.0
Capital charges	54.4	65.9	69.1	91.0
Total annual costs	85.0	104.9	111.5	148.6
Normalized cost per m <sup>3</sup> /day (total annual cost ÷ throughput) (\$/m <sup>3</sup> )	223	110	59	39

Use of the costs for 90 percent control in estimating costs for 50 percent control under Option 1 requires considerable additional assumptions, since the bulk gasoline terminal NSPS and other available sources do not address controls in the 50 percent range. The NSPS control equipment costs do not include direct estimates of the relative costs of condenser and refrigeration equipment, which would vary with control efficiency, and costs of other control components such as the vapor collection system, which would be expected to be relatively constant. For the smallest model gasoline terminal, the breakdown of annualized costs in the first column of Table 3-19 was calculated.

TABLE 3-19. DISTRIBUTION OF ANNUAL COSTS FOR LOADING CONTROL BY REFRIGERATED CONDENSER

	Annual costs for model 380 m <sup>3</sup> /day gasoline terminal (90% control) <sup>47</sup>	Estimated cost reduction for 50 percent control	Estimated costs for 50 percent control relative to 90 percent control
Capital charges	64 percent	0.5	32.0 percent
Electricity	17 percent	0.8	3.4 percent
Maintenance	15 percent	0.5	7.5 percent
Operating labor	4 percent	none	4.0 percent
	100 percent		46.9 percent

To obtain an estimate of the overall cost of a 50 percent control system relative to a 90 percent control system, likely reductions in each cost category associated with the reduced control efficiency (Column 2, Table 3-19) were estimated as follows. IT Enviroscience data indicate that the electricity requirement for condensation systems at 50 percent efficiency is about one-fifth of that for 90 percent control, and that the annual amount for operating labor will be constant regardless of control efficiency.<sup>50</sup> Assuming that condenser emission reduction is proportional to vapor pressure reduction, 50 percent control would require reduction of 90 mm Hg vapor pressure at inlet temperature of 20°C to 45 mm Hg at outlet temperature of about 6°C, while 90 percent control would require about -33° to reduce the vapor pressure to 4.5 mm Hg.

Installed capital costs for condenser systems in one reference indicate that units operating at -33°C are typically about three times as expensive as 6°C units.<sup>51</sup> Although this indicates that the capital cost for condenser and refrigeration system with 50 percent efficiency may be one third of the estimate for 90 percent control, the overall cost of the control equipment and associated maintenance will not be

reduced proportionately since vapor collection systems will not be similarly reduced in cost. Since supporting data on the relative magnitude of collection and condensation costs are not available, it was assumed that the overall capital cost of the control system would be reduced by 50 percent. If costs for the collection and condensation systems were approximately equal, this overall assumption would be equivalent to assuming a one-third reduction in collection system costs in addition to the relatively firm two-thirds reduction in condenser system costs. Maintenance costs were assumed to decrease proportionate to capital costs of the control system, since the bulk gasoline terminal NSPS maintenance cost estimates were consistently about 22 percent of capital costs.<sup>47</sup>

As shown in Table 3-19, the net result of estimated control costs reductions in the four cost categories is to reduce overall annualized costs for 50 percent control to about 47 percent of those estimated for 90 percent control or about \$14,700 for the perchloroethylene co-product model plant. A 50 percent reduction in the estimated capital cost results in a model plant capital cost of \$50,900 for 50 percent control. These costs produce the following net cost and cost-effectiveness figures for 50 percent control of perchloroethylene co-product model plant loading emissions.

Total installed capital cost	\$50,900
Annualized cost	14,700
Recovery credit	(1,000)
Net annualized cost	\$13,700
Emission reduction	2.5 Mg/yr; 50%
Cost-effectiveness	\$ 5,470/Mg

Secondary controls: Combined capital costs for a vapor-balance system for hex-waste handling used on the perchloroethylene co-product process at Plant 6 and a second system to recycle and condense emissions from the vapor-balance system and from waste product storage are estimated

at \$410,000.<sup>52</sup> Sufficient data were not available to estimate costs of the waste caustic steam stripper at Plant 6. Due to the relatively small proportion of total emissions represented by secondary emissions, and the highly plant-specific nature of these emissions and related control costs, no estimate of costs of secondary emission controls was made.

Summary: Table 3-20 summarizes Option 1 model plant control costs for perchloroethylene co-product plants developed in this sub-section. Table 3-21 presents estimated capital and annualized control costs for each plant. These costs were calculated by multiplying model plant costs by the plant capacity factors in Table 3-4, except for process controls at Plant 5 and storage controls at Plants 6 and 9, which were derived individually above.

TABLE 3-20. OPTION 1 PERCHLOROETHYLENE CO-PRODUCT MODEL PLANT CONTROL COSTS

Control type	Control efficiency (%)	Capital cost (\$)	Net annual cost (\$/yr)
Process	90	No model plant costs developed	
Fugitive	42	19,200	10,900
Storage	50	26,300	4,000
	95	285,000	75,700
Loading	50	50,900	13,700
	90	101,700	29,500

TABLE 3-21. OPTION 1 PERCHLOROETHYLENE CO-PRODUCT PLANT  
CONTROL COSTS

Plant	Process	Fugitive	Capital costs (\$)		
			Storage	Loading	Total
4	--	--	541,500	--	541,500
5	6,700	--	387,600	138,300	532,600
6	--	--	675,500 <sup>a</sup>	69,200	744,700 <sup>a</sup>
7	--	--	134,900	261,100	396,000
8	--	--	--	--	--
9	--	8,800	447,500 <sup>a</sup>	--	456,300 <sup>a</sup>
Total	6,700	8,800	2,187,000 <sup>a</sup>	468,600	2,671,100 <sup>a</sup>

Plant	Process	Fugitive	Net annual costs (\$/yr)		
			Storage	Loading	Total
4	--	--	143,800	--	143,800
5	2,100	--	103,000	40,100	145,200
6	--	--	183,200 <sup>a</sup>	18,600	201,800 <sup>a</sup>
7	--	--	20,500	70,300	90,800
8	--	--	--	--	--
9	--	5,000	123,000 <sup>a</sup>	--	128,000 <sup>a</sup>
Total	2,100	5,000	573,500 <sup>a</sup>	129,000	709,600 <sup>a</sup>

<sup>a</sup>Includes joint storage for methane chlorination and perchloroethylene co-product processes at Plants 6 and 9.

-- indicates no optional controls

### 3.5.2 Option 2 Control Costs

This section provides estimates for the Option 2 perchloroethylene co-product plant controls discussed in Section 3.4.

Process controls: Emission reductions for the estimated 90 percent Option 2 process emission control by refrigerated condenser were derived from Tables 3-6 and 3-13. Capital and annualized costs for all plants under Option 2, below, are the same as those for the Plant 5 Option 1 process control, as explained in 3.5.1. This results in the net costs and cost-effectiveness figures shown in Table 3-22.

Installed capital cost	\$6,650
Annualized cost	\$1,930
Utilities and labor	<u>\$ 255</u>
Total annualized costs	\$2,195

TABLE 3-22. NET ANNUALIZED COSTS FOR OPTION 2 CONTROL OF PROCESS EMISSIONS AT PERCHLOROETHYLENE CO-PRODUCT PLANTS

Plant	Emission reduction (Mg/yr)	Recovery credit (\$/yr)	Net annual cost (\$/yr)	Cost effectiveness (\$/Mg)
4	0.19	79	2,116	11,100
5	0.14	59	2,136	15,300
6	0.14	59	2,136	15,300
7	0.53	222	1,973	3,700
8	0.04	17	2,178	54,500
9	0.04	17	2,178	54,500

Fugitive control: The 56 percent control under Option 2 requires equipment specifications for pumps and relief valves to be added to the Option 1 inspection and maintenance program. The total capital cost for such program for the small SOCMI fugitives model plant is about \$30,700, with a corresponding annualized cost of \$18,000.<sup>27</sup> Assuming applicability of these costs to the perchloroethylene co-product model plant (see 3.5.1), net annualized cost and cost-effectiveness are as follows.

Total installed capital cost	<u>\$30,700</u>
Total annualized cost	18,800
Recovery credit for carbon tetrachloride	( <u>4,500</u> )
Net annualized cost	14,300
Emission reduction	10.7 Mg/yr; 56%
Cost-effectiveness	\$ 1,340/Mg

Storage controls: Option 2 storage control costs for the perchloroethylene co-product model plant are identical to those estimated for 95 percent control under Option 1 in 3.5.1. These costs are as follows:

Total installed captial cost	<u>\$285,000</u>
Annualized cost	82,600
Recovery credit	( <u>6,900</u> )
Net annualized cost	75,700
Emission reduction	16.5 Mg/yr; 95%
Cost-effectiveness	\$ 4,600/Mg

For the two-process plants, Option 1 control costs also apply to Plants 6 and 9 for Option 2. The costs for Plant 8, below, were obtained in the same manner as the Option 1 costs for two-process plants, described in 3.5.1. The combined plant capacity factor for Plant 8 is 1.12.

	<u>Plant 6</u>	<u>Plant 8</u>	<u>Plant 9</u>
Installed capital cost	\$675,500	\$319,200	\$447,500
Annualized cost	195,900	92,600	129,700
Recovery credit	(12,700)	(5,300)	(6,700)
Net annual cost	<u>\$183,200</u>	<u>\$ 87,300</u>	<u>\$123,000</u>
Emission reduction	30.3 Mg/yr	12.7 Mg/yr	16.1 Mg/yr
Cost-effectiveness	\$6,050/Mg	\$6,870/Mg	\$7,640/Mg

Loading controls: Model plant costs for Option 2 loading controls at perchloroethylene co-product plants are identical to those for the Option 1 90 percent control level, derived in 3.5.1. These costs are as follows:

Total installed capital cost	<u>\$101,700</u>
Annualized cost	31,300
Recovery credit	<u>(1,840)</u>
Net annualized cost	29,460
Emission-reduction	4.4 Mg/yr; 90%
Cost-effectiveness	\$ 6,700/Mg

Secondary controls: As explained in 3.5.1, no estimate was made of secondary emission control costs.

Summary: Table 3-23 summarizes Option 2 model plant control costs for perchloroethylene co-product plants developed in this sub-section. Table 3-24 presents estimated capital and annualized control costs for each plant. These costs were calculated by multiplying model plant costs by the plant capacity factors in Table 3-4, except for all process controls, and storage controls of Plants 6, 8 and 9, which are derived individually, above.

TABLE 3-23. OPTION 2 PERCHLOROETHYLENE CO-PRODUCT MODEL PLANT CONTROL COSTS

Control type	Control efficiency (%)	Capital cost (\$)	Net annual cost (\$/yr)
Process	90	No model plant costs developed	
Fugitive	56	30,700	14,300
Storage	95	285,000	75,700
Loading	90	101,700	29,500

TABLE 3-24. OPTION 2 PERCHLOROETHYLENE CO-PRODUCT PLANT CONTROL COSTS

Plant	Capital costs (\$)				
	Process	Fugitive	Storage	Loading	Total
4	6,700	58,300	541,500	193,200	799,700
5	6,700	41,800	387,600	138,300	574,400
6	6,700	41,800	675,500 <sup>a</sup>	138,300	862,300 <sup>a</sup>
7	6,700	157,500	1,462,100	521,700	2,148,000
8	6,700	14,100	319,200 <sup>a</sup>	46,800	386,800 <sup>a</sup>
9	6,700	14,100	447,500 <sup>a</sup>	46,800	515,100 <sup>a</sup>
Total	40,200	327,600	3,833,400 <sup>a</sup>	1,085,100	5,286,300 <sup>a</sup>

Plant	Net annual costs (\$/yr)				
	Process	Fugitive	Storage	Loading	Total
4	2,100	27,200	143,800	56,100	229,200
5	2,100	19,400	103,000	40,100	164,600
6	2,100	19,400	183,200 <sup>a</sup>	40,100	244,800 <sup>a</sup>
7	2,000	73,400	388,300	151,300	615,000
8	2,200	6,600	87,300 <sup>a</sup>	13,600	109,700 <sup>a</sup>
9	2,200	6,600	123,000 <sup>a</sup>	13,600	145,400 <sup>a</sup>
Total	12,700	152,600	1,028,600 <sup>a</sup>	314,800	1,508,700 <sup>a</sup>

<sup>a</sup>Includes joint storage for methane chlorination and perchloroethylene co-product processes at Plants 6, 8, and 9.

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40. Reference 28, p. 1-6.
41. Reference 5, Report 5, p. IV-4.
42. Reference 5, Report 5, p. IV-6.
43. Reference 29, Report 1, p. C-16, C-17.
44. Reference 29, Report 1, p. IV-9.
45. Reference 5, Report 2, p. IV-4, and Report 5, p. IV-6.
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47. Reference 30, p. 8-54.

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49. Reference 30, p. 8-41.
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## 4.0 CARBON TETRACHLORIDE PRODUCTION BY METHANE CHLORINATION

This chapter discusses plants which produce carbon tetrachloride by methane chlorination. A brief process description is followed by estimates of uncontrolled emissions, Option 1 and Option 2 controls and emissions, and associated control costs. For plants which use methane chlorination and the perchloroethylene co-product process, assumptions as to the amount of carbon tetrachloride made by each process were addressed in Section 3.2, and will only be mentioned briefly here. Total costs for storage emission control at these plants are estimated in Section 3.5, and will not be addressed in this chapter.

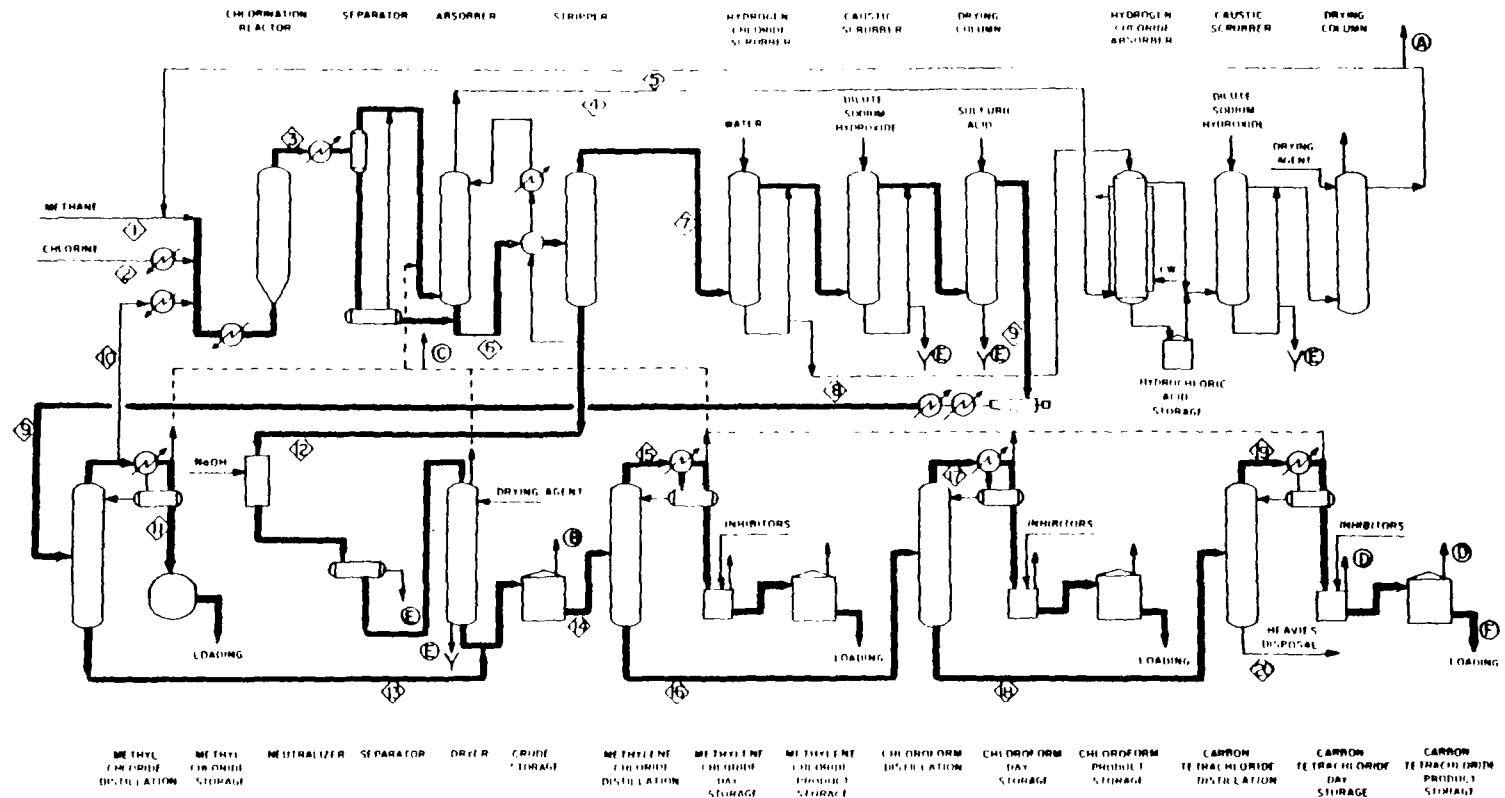
### 4.1 METHANE CHLORINATION PROCESS DESCRIPTION

#### 4.1.1 General Information

As shown in Table 3-1, the two plants using only methane chlorination to produce carbon tetrachloride have the smallest production capacities in the country, totalling 11,000 Mg/yr. An unknown amount of additional production by methane chlorination is included in the 124,000 Mg/yr total capacity for plants also using the perchloroethylene co-product process.

#### 4.1.2 Process Description

In the methane chlorination process, carbon tetrachloride is produced as a co-product with methyl chloride, methylene chloride and chloroform. Methane may be chlorinated thermally, photochemically or catalytically, but typical processes are thermal, operating at about 400°C and 200 kPa. Four sequential distillations remove the various products with additional process steps to handle by-product hydrogen chloride. A typical process flow diagram for methane chlorination is shown in Figure 4-1. Crude products and methyl chloride can be recycled to alter product mixes, but no information is available on the actual product mix at individual plants.



NOTE: Letters in this figure refer to process vents described in the text and tables. Numbers refer to process descriptions in the first reference cited below. Heavy lines indicate final product streams throughout the process.

Figure 4-1. Process flow diagram for methane chlorination process.<sup>1,2</sup>

#### 4.1.3 Carbon Tetrachloride Emission Factors for the Methane Chlorination Process

Table 4-1 gives estimated emission factors for the carbon tetrachloride emission points identified in Figure 4-1.

### 4.2 UNCONTROLLED METHANE CHLORINATION PLANT EMISSIONS

#### 4.2.1 Model Plant

The model plant for the methane chlorination process was chosen to be consistent with those used in previous investigations.<sup>1,2</sup> With a total chloromethanes production capacity of 200,000 Mg/yr divided into 20 percent methyl chloride, 45 percent methylene chloride, 25 percent chloroform and 10 percent carbon tetrachloride, model plant carbon tetrachloride production capacity is 20,000 Mg/yr. The basic model plant configuration is shown in Figure 4-1. More detail on model plant fugitive emission sources and storage facilities is provided in conjunction with cost estimates in Section 4.5. See 3.2.1 for further discussion of model plants.

#### 4.2.2 Capacity Apportionment in Two-Process Plants

As discussed in 3.2.2, a number of assumptions and calculations had to be made regarding the distribution of carbon tetrachloride production capacity between the methane chlorination and perchloroethylene co-product processes at two-process plants. After estimating production by the perchloroethylene co-product process, the following methylene chlorination production capacities were obtained by subtraction: Plant 6: 20,200 Mg/yr, Plant 8: 13,200 Mg/yr, Plant 9: 22,200 Mg/yr (see Table 3-3).

#### 4.2.3 Proportionality and Scales of Production

Throughout the following analysis, direct proportionality of emissions, control efficiencies and costs over all scales of production was assumed. The plant capacity factors in Table 4-2, derived by dividing each plant's assumed methane chlorination process capacity by that of the model plant, were used to apply model plant emission estimates and control costs to each plant. Production capacities for two-process plants were cited above; other were taken directly from Table 3-1.

TABLE 4-1. UNCONTROLLED MODEL PLANT CARBON TETRACHLORIDE EMISSION FACTORS FOR METHANE CHLORINATION PROCESS

Emission source	Source designation <sup>a</sup>	Uncontrolled carbon tetrachloride emission factor <sup>b</sup>
Recycled methane inert gas purge vent	A	<0.042 kg/Mg
In-process storage	B	0.031 kg/Mg
Distillation area emergency inert gas vent	C	0.052 kg/Mg
Process fugitive <sup>c</sup>		4.0 kg/hr
Product storage	D	0.60 kg/Mg
Secondary	E	0.017 kg/Mg
Handling	F	0.24 kg/Mg

<sup>a</sup>Source designation shown in Figure 4-1. A, B, and C are process components.

<sup>b</sup>Emission factors in terms of kg/Mg refer to kg of carbon tetrachloride emitted per Mg of carbon tetrachloride produced. From Reference 3.

<sup>c</sup>Fugitive emissions are independent of production rate.

TABLE 4-2. METHANE CHLORINATION PLANT CAPACITY FACTORS (RELATIVE TO MODEL PLANT)

Plant	Plant capacity factor
1	0.20
3	0.35
6	1.01
8	0.66
9	1.11
Total	3.33

#### 4.2.4 Uncontrolled Emissions

The methane chlorination model plant emissions in Table 4-3 are based on the model plant carbon tetrachloride production capacity of 20,000 Mg/yr and the uncontrolled emission factors presented in Table 4-1. The three process emission sources were combined for the purpose of this analysis. The assumed industry-wide capacity utilization factor of 0.68 (see 3.2.4) and the appropriate plant capacity factors from Table 4-2 were applied to the model plant emission estimates to produce the plant-specific estimates shown in Table 4-4.

TABLE 4-3. METHANE CHLORINATION MODEL PLANT EMISSIONS

Source	Model plant carbon tetrachloride emissions (Mg/yr)
Process	2.50
Fugitive	35.0
Storage	12.0
Loading	4.8
Secondary	0.34
Total	54.6

TABLE 4-4. UNCONTROLLED EMISSIONS FOR METHANE CHLORINATION PLANTS

Plant number	Uncontrolled emission estimates (Mg/yr)					
	Process	Fugitive	Storage	Loading	Secondary	Total
1	0.34	4.8	1.6	0.65	0.05	7.4
3	0.60	8.4	2.9	1.15	0.08	13.1
6	1.72	24.2	8.3	3.31	0.23	37.8
8	1.12	15.8	5.4	2.16	0.15	24.6
9	1.89	26.3	9.0	3.60	0.26	41.0
Total	5.67	79.5	27.2	10.87	0.77	124.0

#### 4.3 OPTION 1 CONTROLS AND EMISSIONS FOR METHANE CHLORINATION PLANTS

Option 1 control efficiencies represent the most stringent of existing, State-required or applicable Group III CTG controls for areas requesting an ozone NAAQS attainment date extension beyond 1982. These controls are discussed individually below as they apply to carbon tetrachloride production by methane chlorination. They are then combined to define Option 1 control efficiencies for each source category at each plant, and used to estimate controlled emissions under Option 1. State regulations and Group III CTGs and associated control efficiencies are discussed in detail in Section 2.2, and existing controls and State regulations applying to methane chlorination plants are included in Tables 3-7 and 3-8. The discussion below is limited to the applicability of controls to given plants and other plant-specific considerations.

##### 4.3.1 Existing Controls

Information on control technology currently in place at carbon tetrachloride production facilities was obtained mainly in telephone conversations with State agency personnel. Some data were available from previous EPA industry surveys. Table 3-7 summarizes the information on existing controls. Control efficiencies were provided either in the cited references, or derived from technical data in them. In most cases, unreported efficiencies were estimated to be proportional to

vapor pressure reductions achieved by given condenser outlet temperatures. The reference reporting 50 percent control for the process vent condenser at Plant 1 did not mention control of in-process storage. Control of the emergency inert gas vent would not be practical, so this control was assumed to apply only to the recycled methane inert gas purge vent (Table 4-1), which would result in about 17 percent control of overall process emissions. Since the existing storage tank condenser at Plant 3 was reportedly brine-cooled, a condenser outlet temperature of 5°C was assumed, which would provide 50 percent control of carbon tetrachloride emissions.

#### 4.3.2 State Regulations

As shown in Table 3-8, the only State regulations which can be assumed to provide some emission control at methane chlorination plants are storage control requirements at Plants 6 and 9 (50 and 95 percent), and loading control requirements at Plant 6 (50 percent). Texas process control requirements are not applicable to methane chlorination process vents at Plant 6, since the VOC in this vent stream includes only methane and chlorinated organics,<sup>6</sup> which are not covered by the list of affected compounds given in Section 2.2.1. Applicability of the Texas loading regulation is discussed in 3.3.2.

#### 4.3.3 Group III Control Techniques Guidelines

Table 3-9 summarizes the current ozone NAAQS status of counties in which carbon tetrachloride production facilities are located. Of the plants using methane chlorination, the Group III CTGs (2.2.2) are assumed to require 42 percent control of fugitive emissions and 95 percent of storage emissions at Plants 3 and 9, due to extensions beyond 1982 for these areas.

#### 4.3.4 Combined Option 1 Controls

Table 4-5 summarizes control efficiencies applicable to methane chlorination plants for the Option 1 controls described in 4.3.1, 4.3.2, and 4.3.3. Table 4-6 provides more detail on the storage emission controls involved. The most stringent level of storage control for each plant was selected as the Option 1 storage control shown in Table 4-5.

TABLE 4-5. OPTION 1 CONTROL SUMMARY FOR METHANE CHLORINATION PLANTS

Plant	Process	Option 1 control efficiency (percent)			
		Fugitive	Storage	Loading	Secondary
1	17	--	--	--	--
3	--	42	95	--	--
6	--	--	95	50	--
8	--	--	--	--	--
9	--	42	95	--	--

TABLE 4-6. OPTION 1 CONTROLS FOR STORAGE EMISSIONS AT METHANE CHLORINATION PLANTS

Plant	Existing control	Current regulations	Group III CTG
1	--	--	--
3	50	--	95
6	95	50	--
8	--	--	--
9	--	95	95

#### 4.3.5 Estimated Option 1 Emissions

Applying control efficiencies in Table 4-5 to uncontrolled emission estimates (Table 4-4) produced the Option 1 controlled emission estimates in Table 4-7.

TABLE 4-7. OPTION 1 CONTROLLED EMISSIONS FOR METHANE CHLORINATION PLANTS

Plant	Process	Option 1 controlled emissions (Mg/yr)					Total
		Fugitive	Storage	Loading	Secondary		
1 .	0.28	4.8	1.6	0.65	0.05	7.4	
3	0.60	4.9	0.1	1.15	0.08	6.8	
6	1.72	24.2	0.4	1.66	0.23	28.2	
8	1.12	15.8	5.4	2.16	0.15	24.6	
9	1.89	15.3	0.5	3.60	0.26	21.6	
Total	5.61	65.0	8.0	9.22	0.77	88.6	
Option 1 control efficiency (%)	1	18	70	15	--	29	

#### 4.4 OPTION 2 CONTROLS AND EMISSIONS FOR METHANE CHLORINATION PLANTS

This section describes the estimated best control (EBC) used in Option 2, and estimates the emissions expected after application of these controls to methane chlorination plants.

##### 4.4.1 Estimated Best Controls

The following control methods were selected as EBC for carbon tetrachloride plants using the methane chlorination process. All control efficiencies are specific to carbon tetrachloride.

Process emissions: IT Enviroscience performed preliminary design for a chloroform-based absorption system operating at -40°C and 200 kPa, which was estimated to provide 92 percent control of the inert gas purge vent and in-process storage.<sup>7</sup> The intermittent nature of the emergency inert gas vent emissions makes known controls impractical. Improved process control may be a feasible method of reducing these emissions, but sufficient information was not available to permit assessment of this type of approach. Applying 92 percent control to model plant inert gas purge vent and in-process storage emissions, and assuming no control of the emergency inert gas vent, yields an overall process control efficiency of 62 percent.

Fugitive emissions: It was estimated that an inspection and repair program similar to the Group III CTG can provide 42 percent control,<sup>8</sup> and that EBC would include addition of equipment specifications for pumps, compressors and relief valves, which can raise this to 56 percent control.<sup>9</sup>

Storage emissions: Vapor recovery and -20°C refrigerated condenser systems can control carbon tetrachloride storage emissions at efficiencies up to 95 percent.<sup>6,10,11</sup>

Loading emissions: Vapor recovery, refrigerated condensers and tank truck leakage reduction measures are estimated to provide 90 percent control of loading emissions.<sup>12,13</sup>

Secondary emissions: Secondary emission sources include waste caustic from three process locations, sulfuric acid and high density salt solution from two different dryers, and heavies from distillation. Controls for these emissions could not be developed due to lack of technical data, and it appears that existing control techniques would be impractical for these disparate sources.

#### 4.4.2 Estimated Option 2 Emissions

Table 4-18 summarizes annual emissions and control efficiencies which can be achieved by methane chlorination plants with the Option 2 controls described in 4.4.1.

TABLE 4-8. OPTION 2 CONTROLLED EMISSIONS FOR METHANE CHLORINATION PLANTS

Plant	Process	Option 2 controlled emissions (Mg/yr)					Total
		Fugitive	Storage	Loading	Secondary		
1	0.13	2.1	0.08	0.06	0.05	2.4	
3	0.23	3.7	0.15	0.12	0.08	4.3	
6	0.65	10.6	0.42	0.33	0.23	12.2	
8	0.43	7.0	0.27	0.22	0.15	8.1	
9	0.72	11.6	0.48	0.36	0.26	13.4	
Total	2.16	35.0	1.37	1.09	0.77	40.4	
Option 2 control efficiency (%)	62	56	95	90	--	67	

## 4.5 CONTROL COSTS FOR METHANE CHLORINATION PLANTS

This section estimates control costs for the Option 1 and Option 2 controls discussed in this chapter. Model plant costs are developed for each source category and plant-specific costs for Options 1 and 2 are presented under summary headings at the end of 4.5.1 and 4.5.2. Costing methodology and assumptions are discussed in Chapter 1. All costs are in July 1982 dollars except where noted. Examples and details of control requirement calculations are presented in Appendix B. Storage control costs for Plants 6, 8 and 9 were estimated in Section 3.5, and are not addressed in this section.

### 4.5.1 Option 1 Control Costs

This section provides cost estimates for the Option 1 methane chlorination plant controls discussed in 4.3.4.

Process controls: The only Option 1 process emission control for methane chlorination is a 50 percent efficiency refrigerated condenser on the process vents at Plant 1. The following analysis uses the only available detailed emissions data, which are for Plant 6, to arrive at model plant control costs which can then be scaled to the size of Plant 1. Process data presented in Appendix B-2 result in a calculated flow rate of  $87 \text{ ft}^3/\text{min}$  and the following estimates of emissions and recovery credit for Plant 6.

TABLE 4-9. EMISSIONS AND RECOVERY CREDITS FOR 50 PERCENT METHANE CHLORINATION PROCESS CONTROL AT PLANT 6

VOC component	Uncontrolled emission rate (Mg/yr)	50% emission reduction (Mg/yr)	Price <sup>14</sup> (\$/Mg)	Recovery credit (\$/yr)
Methyl chloride	389	194	435	84,390
Methylene chloride	9.8	4.9	528	2,590
Chloroform	0.6	0.3	682	200
Carbon tetrachloride	0.8	0.4	418	170
	1,297	199.6		87,350

Since the methane chlorination process capacity at Plant 6 is only 1 percent larger than that of the model plant, the recovery credits and emission reductions above were used directly in the following model plant cost analysis. IT Enviroscience estimated control costs for 50 percent control of a VOC stream of similar molecular weight and flow rate, for VOC concentrations from 2 to 20 percent, as follows:

TABLE 4-10. CONTROL COST SUMMARY FOR 50 PERCENT VOC REMOVAL BY REFRIGERATED CONDENSER<sup>15</sup>  
(Molecular weight = 60; Flow rate = 100 ft<sup>3</sup>/min)

VOC concentration (%)	Total installed capital cost (\$)	Annualized capital cost (\$/yr)	Electricity (\$/yr)	Labor (\$/yr)
20	104,600	30,400	100	16,600
10	79,200	23,100	100	16,600
5	64,500	18,700	100	16,600
2	53,100	15,400	100	16,600

The capital costs include all battery-limit costs for new equipment and a contingency allowance of 30 percent. Linear projection of these capital costs to a VOC concentration of 30 percent gives an approximate capital cost of \$130,000 and an annualized cost of \$38,000. Electricity and labor were assumed to be constant. It was further assumed that use of a 100 ft<sup>3</sup>/min unit for an 87 ft<sup>3</sup>/min flow rate would be appropriate. Model plant costs and credits for all VOC recovery at full capacity and for carbon tetrachloride recovery alone at estimated 0.68 capacity utilization are as follows:

Installed capital cost	<u>\$130,000</u>
Annualized cost	\$ 38,000
Utilities and labor	<u>\$ 16,700</u>
Total annualized costs	\$ 54,700

For all VOC (at full production):

Recovery credit	<u>\$(87,350)</u>
Net annualized cost (credit)	(32,650)
Emission reduction	200 Mg/yr; 50%
Cost-effectiveness (credit)	<u>\$(163)/Mg</u>

For carbon tetrachloride (at 0.68 capacity utilization):

Recovery credit	\$(-120)
Net annualized cost	\$ 54,580
Emission reduction	0.3 Mg/yr; 50%
Cost-effectiveness	\$ 182,000/Mg

The net annualized cost of \$54,580 for 50 percent control by refrigerated condenser estimated above is greater than the cost estimated for 92 percent control by an absorption system in Option 2, below. This may be due to potential overestimation in the Option 1 cost derivation, or the better efficiency achieved by the less expensive proposed Option 2 control. Since the Option 1 cost estimate is for an existing control system, it was assumed the possibility of more efficient controls is not relevant. A plant size scaling factor of 0.20 results in a net annualized Option 1 process control cost for Plant 1 of \$10,920 and an estimated total installed capital cost of \$26,000, for 50 percent control by refrigerated condensation.

Fugitive controls: Based on the totals for model plant fugitive emission sources and process descriptions from IT Enviroscience,<sup>16</sup> estimates of fugitive sources in carbon tetrachloride service at methane chlorination plants were made. Comparison of these carbon tetrachloride sources to the medium-sized model plant in the SOCMi fugitive CTG in Table 4-11 indicates that a capital cost of \$43,300 and an annual cost of \$34,800 for the CTG inspection and maintenance program<sup>8</sup> would be appropriate for Option 1 costs for the methane chlorination model plant. With an emission reduction based on 0.68 capacity utilization, this results in the following model plant cost analysis.

TABLE 4-11. MODEL PLANT FUGITIVE EMISSION SOURCES

	Methane chlorination model plant Total fugitive sources <sup>16</sup>	In carbon tetrachloride service	Medium SOCMF fugitives model plant <sup>17</sup>
Pumps	80	36	29
Process valves	1,930	840	926
Relief valves	70	6	46
Compressor	1	0	2
Capital cost		\$43,300	
Annualized cost		34,800	
Recovery credit for carbon tetrachloride		(4,180)	
Net annualized cost		\$30,620	
Emission reduction		10.0 Mg/yr; 42%	
Cost-effectiveness		\$3,060/Mg (cost)	

Storage controls: This discussion covers only Option 1 control costs for storage facilities at Plants 1 and 3, since the two-process plants (Plants 6, 8 and 9) are covered in Section 3.5. The following Option 1 storage control cost estimates for the methane chlorination model plant are based on the costs in Table 3-17, which are explained in Section 3.5.

Total installed capital cost	<u>\$285,000</u>
Annualized cost	82,600
Recovery credit	(3,300)
Net annualized cost	79,300
Emission reduction	7.8 Mg/yr; 95 percent
Cost-effectiveness	\$10,166/Mg

Loading controls: The basis for the derivation of annual and capital costs for loading control is explained in 3.5.1. From Figure 3-3, July 1982 total annualized costs for 90 percent control of methane chlorination model plant loading emissions can be estimated at \$23,200. Assuming 65 percent of the total annual cost as capital charges and an annualized capital cost factor of 0.20 results in a corresponding capital cost of \$75,400. The following annual and capital cost estimates for the 50 percent Option 1 level were derived from these 90 percent control costs using the same methods described in 3.5.1. From Table 3-19, the 50 percent control annual cost was assumed to be 47 percent of that for 90 percent control, or \$10,900. Based on 50 percent reduction of capital costs, the corresponding capital cost is estimated at \$37,700.

Total installed capital cost	<u>\$37,700</u>
Annualized cost	\$10,900
Recovery credit	<u>(670)</u>
Net annualized cost	10,230
Emission reduction	1.6 Mg/yr; 50%
Cost-effectiveness	\$ 6,400/Mg

Secondary controls: No secondary emission controls were identified for methane chlorination plants.

Summary: Table 4-12 summarizes Option 1 model plant control costs for methane chlorination plants developed in this sub-section. Table 4-13 presents estimated capital and annualized control costs for each plant. These costs were calculated by multiplying model plant costs by the plant capacity factors in Table 4-2.

TABLE 4-12. OPTION 1 METHANE CHLORINATION MODEL PLANT CONTROL COSTS

Control type	Control efficiency (%)	Capital cost (\$)	Net annual cost (\$/yr)
Process	17	130,000	54,600
Fugitive	42	43,300	30,600
Storage	95	285,000	79,300
Loading	50	37,700	10,230

TABLE 4-13. OPTION 1 METHANE CHLORINATION PLANT CONTROL COSTS

Plant	Capital costs (\$)				Total
	Process	Fugitive	Storage	Loading	
1	26,000	--	--	--	26,000
3	--	15,200	99,800	--	115,000
6	--	--	a	38,100	38,100 <sup>a</sup>
8	--	--	--	--	--
9	--	48,200	a	--	48,200
Total	26,000	63,400	99,800 <sup>a</sup>	38,100	227,300 <sup>a</sup>

Plant	Net annual costs (\$/yr)				Total
	Process	Fugitive	Storage	Loading	
1	10,900	--	--	--	10,900
3	--	10,700	27,800	--	38,500
6	--	--	a	10,300	10,300 <sup>a</sup>
8	--	--	--	--	--
9	--	34,000	a	--	34,000 <sup>a</sup>
Total	10,900	44,700	27,800 <sup>a</sup>	10,300	93,700 <sup>a</sup>

<sup>a</sup>Storage at Plants 6 and 9 was addressed in Chapter 3 and is not included here.

-- indicates no Option 1 control

#### 4.5.2 Option 2 Control Costs

This section provides estimates of the Option 2 methane chlorination plant controls discussed in Section 4.4.

Process controls: The Option 2 control for the methane chlorination process was based on a preliminary chloroform absorber design by IT Enviroscience, which included the following capital and annualized cost estimates for the model methane chlorination plant:<sup>18</sup>

Total installed capital cost	<u>\$165,000</u>
Annualized cost	\$ 47,900
Utilities	<u>\$ 1,500</u>
Total annualized cost	\$ 49,400
Recovery credit	<u>(\$220,400)</u>
Net annualized cost (credit)	(\$171,000)
Emission reduction	504 Mg/yr; 92%
Cost-effectiveness (\$ per Mg emission reduction)	(\$339/Mg) (savings)

The recovery credit cited above is based on the value of the net recovery of methyl chloride (97.1 percent), methylene chloride (2.4 percent), chloroform (0.2 percent), and carbon tetrachloride (0.2 percent), which are recycled to the process.<sup>19</sup> Since this absorber does not control the emergency inert gas vent, it applies only to the 1.46 Mg/yr of the 2.50 Mg/yr total model plant process emissions which are due to the controlled purge vent and in-process storage (see Tables 4-1 and 4-3). The 92 percent efficiency of the absorber on these two sources produces 62 percent control of total carbon tetrachloride process emissions. With 0.68 capacity utilization, this results in a net emission control of about 0.91 Mg/yr of carbon tetrachloride for the model plant. The following analysis would apply to the model plant:

Total annualized cost	\$49,400
Recovery credit for carbon tetrachloride	(\$ 380)
Net annualized cost	\$49,020
Emission reduction	0.91 Mg/yr; 92%
Cost-effectiveness	\$53,900/Mg (cost)

Fugitive control: Option 2 adds equipment specifications for pumps and relief valves to the Option 1 inspection and maintenance program, for a total control efficiency of 56 percent. The total capital cost of such a program for the medium-size SOCMI fugitives model plant is \$77,600, with a corresponding annualized cost of \$50,700.<sup>9</sup> Assuming applicability of these costs to the methane chlorination model plant (see 4.5.1), the following net cost and cost-effectiveness were derived.

Total installed capital cost	\$77,600
Annualized cost	50,700
Recovery credit for carbon tetrachloride	(\$ 5,560)
Net annualized cost	45,140
Emission reduction	13.3 Mg/yr; 56%
Cost-effectiveness	\$ 3,394/Mg (cost)

Storage controls: This discussion covers only the Option 2 control costs for Plants 1 and 3, since the two-process plants (Plants 6, 8 and 9) were covered in Section 3.5. The following Option 2 storage control cost estimates for the methane chlorination model plant are based on the costs in Table 3-17, which are explained in Section 3.5. They are identical to Option 1 control costs presented in 4.5.1.

Total installed capital cost	<u>\$285,000</u>
Annualized cost	82,600
Recovery credit	<u>(3,300)</u>
Net annualized cost	79,300
Emission reduction	7.8 Mg/yr; 95 percent
Cost-effectiveness	\$ 10,166/Mg

Loading controls: The basis for the derivation of annual and capital costs for loading control is explained in 3.5.1. From Figure 3-3, July 1982 total annualized costs for 90 percent control of loading emissions at the methane chlorination model plant can be estimated at \$23,200, with a corresponding capital cost of \$75,400. These costs result in the following net cost and cost-effectiveness figures, based on 90 percent control of model plant emissions (Table 4-3) and 0.68 capacity utilization.

Total installed capital cost	<u>\$75,400</u>
Annualized cost	23,200
Recovery credit	<u>(1,200)</u>
Net annualized cost	22,000
Emission reduction	2.9 Mg/yr; 90%
Cost-effectiveness	\$7,586/Mg

Secondary controls: No feasible controls were identified for control of secondary emissions at methane chlorination plants.

Summary: Table 4-14 summarizes Option 2 model plant control costs for methane chlorination plants developed in this sub-section. Table 4-15 presents estimated capital and annualized control costs for each plant, calculated by multiplying model plant costs by the plant capacity factors in Table 3-4.

TABLE 4-14. OPTION 2 METHANE CHLORINATION MODEL PLANT CONTROL COSTS

Control type	Control efficiency (%)	Capital cost (\$)	Net annual cost (\$/yr)
Process	62	165,000	49,000
Fugitive	56	77,600	45,100
Storage	95	285,000	79,300
Loading	90	75,400	22,000

TABLE 4-15. OPTION 2 METHANE CHLORINATION PLANT CONTROL COSTS

Plant	Capital costs (\$)				Total
	Process	Fugitive	Storage	Loading	
1	33,000	15,500	57,000	15,100	120,600
3	57,800	27,200	99,800	26,400	211,200
6	166,700	78,400	a	76,200	321,300 <sup>a</sup>
8	108,900	51,200	a	49,800	209,900 <sup>a</sup>
9	183,200	86,100	a	83,700	353,000 <sup>a</sup>
Total	549,600	258,400	156,800 <sup>a</sup>	251,200	1,216,000 <sup>a</sup>

Plant	Net annual costs (\$/yr)				Total
	Process	Fugitive	Storage	Loading	
1	9,800	9,000	15,900	4,400	39,100
3	17,200	15,800	27,800	7,700	68,500
6	49,500	45,600	a	22,200	117,300 <sup>a</sup>
8	32,300	29,800	a	14,500	76,600 <sup>a</sup>
9	54,400	50,100	a	24,400	128,900 <sup>a</sup>
Total	163,200	150,300	43,700 <sup>a</sup>	73,200	430,400 <sup>a</sup>

<sup>a</sup>Storage at Plants 6, 8, and 9 was addressed in Chapter 3 and is not included here.

#### 4.6 REFERENCES

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19. Reference 2, Report 5, p. IV-4.

## 5.0 CARBON TETRACHLORIDE PRODUCTION BY CARBON DISULFIDE CHLORINATION

This chapter discusses the one domestic plant known to produce carbon tetrachloride by chlorination of carbon disulfide. A brief process description is followed by estimates of uncontrolled emissions, Option 1 and Option 2 controls and emissions, and control costs.

### 5.1 CARBON DISULFIDE PROCESS DESCRIPTION

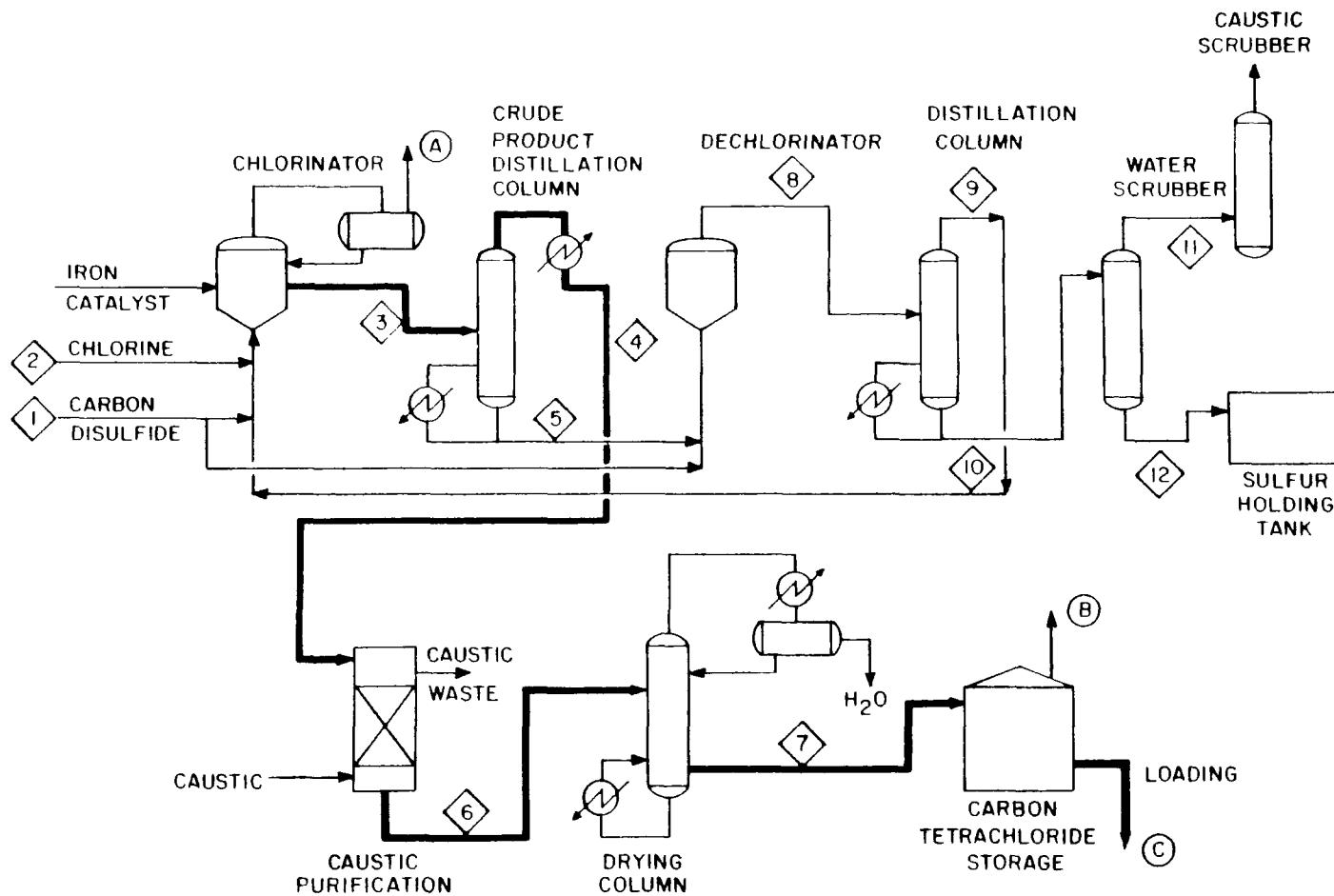
#### 5.1.1 General Information

As shown in Table 3-1, the Stauffer plant at LeMoyne, Alabama (Plant 2), is the only domestic plant producing carbon tetrachloride by chlorination of carbon disulfide. The 91,000 Mg/yr production capacity of this plant is the second largest in the U.S. Two other carbon disulfide-based plants (FMC Corp. at South Charleston, WV, and Stauffer at Niagara Falls, NY) have been closed down since 1975, but formerly had production capacities from 75,000 to 150,000 Mg/yr.<sup>1</sup>

#### 5.1.2 Process Description

In the carbon disulfide chlorination process, a solution of carbon disulfide and sulfur chloride in carbon tetrachloride is fed to a chlorination reactor where chlorine is sparged through the solution to yield a mixture of carbon tetrachloride and sulfur chloride. Crude product carbon tetrachloride is distilled off, purified and dried. The sulfur chloride is then reacted with carbon disulfide, producing carbon tetrachloride and elemental sulfur. The carbon tetrachloride produced in this reaction and excess carbon disulfide are recycled to the chlorination reactor.<sup>2,3</sup> Figure 5-1 is a process flow diagram for Plant 2.

5-2



NOTE: Letters in this figure refer to process vents described in the text and tables. Numbers refer to process descriptions in the first reference cited below. Heavy lines indicate final product streams throughout the process.

Figure 5-1. Process flow diagram for carbon disulfide chlorination process.<sup>2,3,4</sup>

### 5.1.3 Carbon Tetrachloride Emission Factors for the Carbon Disulfide Process

Table 5-1 gives estimated emission factors for the Stauffer/LeMoyne plant emission points shown in Figure 5-1. Existing emission factors<sup>5</sup> were reviewed, and new information on process emission controls was used to produce an uncontrolled process emission factor. Information submitted to the State of Alabama by Stauffer<sup>6</sup> indicates that the existing two-stage condenser has an efficiency of 95 percent. A source test indicated controlled carbon tetrachloride emissions of 55 kg/hr. Uncontrolled emissions would thus be in the range of 1090 kg/hr or 9,560 Mg/yr. Based on production at the time of the test (81,800 Mg/yr), an uncontrolled emission factor of 117 kg/Mg was calculated. As discussed further in 5.3.1, there may be some question as to the degree to which this existing condenser should be considered a process component rather than an emission control. The cost analysis (5.5.1) shows a very favorable product recovery credit.

TABLE 5-1. UNCONTROLLED CARBON TETRACHLORIDE EMISSION FACTORS FOR CARBON DISULFIDE CHLORINATION PROCESS

Emission source	Source designation <sup>a</sup>	Uncontrolled carbon tetrachloride emission factor <sup>b</sup>
Process	A	117 kg/Mg
Storage	B	0.81 kg/Mg
Handling	C	0.24 kg/Mg
Fugitive		0.60 kg/Mg

<sup>a</sup>Source designation shown in Figure 5-1.

<sup>b</sup>Emission factors in terms of kg/Mg refer to kg of carbon tetrachloride emitted per Mg of carbon tetrachloride produced. From Reference 5, except Source A, as described in the text.

## 5.2 UNCONTROLLED CARBON DISULFIDE PLANT EMISSIONS

The uncontrolled emission estimates in Table 5-2 were developed for Plant 2. These estimates are based on a production capacity of 91,000 Mg/yr (Table 3-1), the assumed industry-wide capacity utilization factor of 0.68 (see 3.2.4) and full-production uncontrolled emission factors from Table 5-1.

TABLE 5-2. UNCONTROLLED EMISSION ESTIMATES FOR THE CARBON DISULFIDE PLANT

Plant	Process	Uncontrolled emissions (Mg/yr)			Total
		Fugitive	Storage	Loading	
2	7,240	37	50	15	7,342

## 5.3 OPTION 1 CONTROLS AND EMISSIONS FOR THE CARBON DISULFIDE PLANT

The Group III CTGs do not apply to Plant 2, so this section discusses existing controls and applicable Alabama regulations and then applies them to estimate Option 1 controlled emissions.

### 5.3.1 Existing Controls

The only reported existing emission control at Plant 2 is the refrigerated condenser on the chlorination reactor cited in 5.1.3, which is reported to reduce uncontrolled emissions by 95 percent. The resulting reduction in the controlled process emissions is shown in Table 5-3. The existing condenser might be considered a basic process unit rather than an emission control. Without it, about 10 percent of total carbon tetrachloride production would be lost as emissions, along with other components of the vent stream. Its high product recovery and cost-effectiveness are shown in the control cost analysis (5.5.1). For this assessment, however, the existing condenser has been treated strictly as a control device.

### 5.3.2 State Regulations

Alabama regulations do exist for VOC storage and loading, as indicated in Chapter 2, but submerged fill and the additional loading line controls, which are minimal requirements in these regulations, were included in

the uncontrolled emission factors for storage and loading since these controls were assumed to be standard industry practice. Thus they provide no additional control over the emissions shown in Table 5-2.

### 5.3.3 Combined Option 1 Controls

The existing condenser on the chlorination reactor is the only control relevant to Option 1, providing 95 percent control of process emissions.

### 5.3.4 Estimated Option 1 Emissions

Table 5-3 provides estimated Option 1 emissions, which reflect 95 percent control of the uncontrolled process emissions in Table 5-2.

TABLE 5-3. OPTION 1 CONTROLLED EMISSIONS FOR THE CARBON DISULFIDE PLANT

Plant	Process	Option 1 emissions (Mg/yr)			Total
		Fugitive	Storage	Loading	
2	362	37	50	15	464
Option 1 control efficiency (%)	95	--	--	--	94

## 5.4 OPTION 2 CONTROLS AND EMISSIONS FOR THE CARBON DISULFIDE PLANT

This section describes the estimated best controls (EBC) used in Option 2, and estimates the emissions expected after application of these controls to Plant 2.

### 5.4.1 Estimated Best Controls

The following control methods were selected as EBC for the carbon disulfide plant.

Process emissions: Control assessments were performed for additional refrigerated condensation of the existing -20°C condenser outlet stream, to -40°C and -62°C. Use of retrofit units at these temperatures would provide 74 and 95 percent additional control, increasing the total process control from 95 percent to 98.7 and 99.8 percent, respectively. These theoretical control efficiencies were calculated from the reduction in carbon tetrachloride's vapor pressure corresponding to each condenser's outlet temperature, as shown in Table 5-4. The theoretical -62°C condensation requirement appears feasible with a retrofit cascade-type refrigeration system (costs are estimated in 5.5.2). Thus the additional 95 percent control over emissions with the existing condenser, or 99.8 percent net control, was chosen as Option 2.

Fugitive emissions: Combination of an inspection and repair program and equipment specifications, can achieve a total control efficiency of 56 percent.<sup>7</sup>

Storage emissions: Vapor recovery and a -20°C refrigerated condenser system can control carbon tetrachloride storage emissions at efficiencies up to 95 percent.<sup>8,9,10</sup>

Loading emissions: Vapor recovery, refrigerated condensers and tank truck leak reduction measures are estimated to provide 90 percent control of loading emissions.<sup>11,12</sup>

### 5.4.2 Estimated Option 2 Emissions

Based on control efficiencies of estimated best controls cited in 5.4.1, controlled emissions were estimated for Option 2, as shown in Table 5-5.

TABLE 5-4. OPTION 2 PROCESS CONTROLS FOR THE CARBON DISULFIDE PLANT

	Outlet temperature (°C)	Carbon tetrachloride vapor pressure (mm Hg)	Estimated carbon tetrachloride control relative to uncontrolled case (%)	Estimated carbon tetrachloride control relative to existing emissions (%)
Uncontrolled	40.5 (105°F)	210	--	--
<u>Option 1</u>				
Existing condenser	-20 (-4°F)	10.4	95	--
<u>Option 2</u>				
-40°C condenser	-40 (-40°F)	2.7	98.7	74
-62°C condenser	-62 (-80°F)	0.48	99.8	95

TABLE 5-5. OPTION 2 CONTROLLED EMISSIONS FOR THE CARBON DISULFIDE PLANT

Plant	Option 2 controlled emissions (Mg/yr)				
	Process	Fugitive	Storage	Loading	Total
2	18	16	2	1	37
Option 2 control efficiency (%)	99.8	56	95	90	99

## 5.5 CONTROL COSTS FOR THE CARBON DISULFIDE PLANT

This section estimates control costs for the Option 1 and Option 2 controls discussed in this chapter. Since only one plant is involved, costs were developed directly without a model plant approach. All costs are for July 1982. Examples and details of control requirement calculations are presented in Appendix B.

### 5.5.1 Option 1 Control Costs

This section provides cost estimates for the only Option 1 carbon disulfide plant control, the process condenser discussed in 5.3.3.

Process control: The refrigeration requirement for the existing -20°C condenser is calculated in Appendix B-3 as about 28 tons. The installed capital cost of such a condenser is estimated at \$55,000, excluding coolant/product piping.<sup>13</sup> A total installation cost factor of 0.61<sup>14</sup> was reduced to 0.30, assuming piping is about half of the total installation cost factor. This results in an installed capital cost of \$71,500. Annualized costs were based on a 29 percent factor which was developed specifically for condensers, and include maintenance (6 percent); taxes, insurance, and administration (5 percent); and capital recovery (18 percent).<sup>15</sup> Utility costs were based on approximate usage rates per ton of cooling capacity (3 gpm/ton cooling water; 1.5 KW/ton electricity usage at -20°C)<sup>13</sup>, at \$0.109 per 1000 gallons and \$0.083 per kilowatt-hour (see Appendix B-3). Operating labor is based on \$19/hour and 10 percent of operating time (i.e., 876 hours/year).<sup>15</sup> Recovery credit is based only on carbon tetrachloride emission reduction at 0.68 capacity utilization from Tables 5-2 and 5-3, although consideration of concurrent control of carbon disulfide and sulfur chloride would increase credits.

Total installed capital cost	<u>\$71,500</u>
Annualized cost	20,700
Electricity	29,000
Water	4,800
Operating labor	<u>16,000</u>
Total annualized cost	71,100
Recovery credit (CCl <sub>4</sub> only)	<u>(2,875,000)</u>
Net annualized cost (credit)	(2,804,000)
Emission reduction	6,878 Mg/yr; 95%
Cost-effectiveness (credit)	(\$408/Mg)

### 5.5.2 Option 2 Control Costs

This section provides cost estimates for Option 2 disulfide plant controls discussed in Section 5.4.

Process control: As described in Appendix B-3, it is estimated that a secondary condenser at -62°C can provide 95 percent control of the emissions from the existing process condenser, resulting in a net control of 99.8 percent over estimated uncontrolled emissions. The costs below assume that the existing condenser is in place, and do not include Option 1 costs. Thus the Option 2 costs and cost-effectiveness shown below are incremental relative to Option 1. The capital cost for the retrofit condenser of \$90,000 was obtained from an equipment manufacturer because a published cost estimate was not available for this specialized unit.<sup>16</sup> The installed capital cost is based on an additional 18 percent for taxes, freight and instrumentation and a 61 percent factor for indirect and direct installation costs.<sup>14</sup> Annualized costs were based on a 29 percent factor which was developed specifically for condensers, and includes maintenance (6 percent); taxes, insurance, and administration (5 percent); and capital recovery (18 percent).<sup>15</sup> Utility costs were based on approximate usage rates per ton of cooling capacity (3 gpm/ton

cooling water; 15 KW/ton electricity usage at -62°C),<sup>13</sup> at \$0.109 per 1000 gallons and \$0.082 per kilowatt-hour. Operating labor is based on \$19/hour and 10 percent of operating time (i.e., 876 hours/year).<sup>15</sup> These cost estimates are based on the same cost factors as the previously-addressed condensers for the perchloroethylene co-product and methane chlorination processes, except for utility costs. Utility costs were estimated as described in Appendix B-3. Previously-used cost estimates could not be applied directly. Recovery credits are based only on carbon tetrachloride emission reductions at 0.68 capacity utilization (see Tables 5-2 and 5-5), although consideration of concurrent control of carbon disulfide and sulfur chloride would increase credits.

Total installed capital cost	<u>\$171,000</u>
Annualized cost	49,600
Electricity	25,200
Water	400
Operating labor	<u>16,600</u>
Total annualized cost	91,800
Recovery credit (CCl <sub>4</sub> only)	<u>(143,800)</u>
Net annualized cost (credit)	( 52,000)
Emission reduction	344 Mg/yr; 99.8%
Cost-effectiveness (credit)	(\$151/Mg)

Fugitive control: The best available information on components of the carbon disulfide process is depicted in the process flow diagram presented in Figure 5-1. Since this does not include data on the number of process valves, pumps and other fugitive emission sources, it was assumed that approximate control costs could be derived from the Option 2 costs already presented for the perchloroethylene co-product model plant in 3.5.2. The sections of these two processes in carbon tetrachloride service consist of similar process units (reactor, condenser, crude product distillation/dechlorination, carbon tetrachloride drying/distillation), each with about ten process flow lines in carbon tetrachloride service. These similarities indicate that the number of necessary pumps and

valves in carbon tetrachloride service should be about the same for these two processes. Thus control costs developed for perchloroethylene co-product model plant were used with an annual carbon disulfide plant fugitive emission reduction estimate corresponding to 0.68 capacity utilization in the following cost calculations for Option 2 control.

Total installed capital cost	<u>\$30,700</u>
Annualized cost	18,800
Recovery credit for carbon tetrachloride	<u>(8,800)</u>
Net annualized cost	10,000
Emission reduction	21 Mg/yr; 56%
Cost-effectiveness	\$477/Mg (cost)

Storage control: The storage tank inventory reported for the Stauffer plant at LeMoyne, Alabama is shown in Table 5-6. The number of turnovers per year for the larger tanks were calculated by assuming evenly distributed throughput of the plant's annual production capacity and average tank use at half of capacity. The turnover rates of the smaller tanks were not estimated due to lack of information on their uses, but they are probably intermediate product storage or check tanks with relatively high turnover rates.

TABLE 5-6. CARBON DISULFIDE PLANT STORAGE

	Number of tanks <sup>6</sup>	Size (m <sup>3</sup> ) <sup>6</sup>	Turnovers per year
Carbon tetrachloride	2	869	20
Carbon tetrachloride	2	1,739	20
Carbon tetrachloride	2	60	--
Carbon tetrachloride	1	68	--

Condenser size and control costs for the tanks in Table 5-6 would be in the range of those developed by IT Enviroscience for the large model storage tank ( $2840\text{ m}^3$ , 24 turnovers per year).<sup>17</sup> IT Enviroscience's Case 2 and Case 3 annual cost estimates for the large tank were slightly more than twice those for the  $660\text{ m}^3$  tank used to derive Figure 3-2 and Table 3-17.<sup>18</sup> Thus it was assumed that Option 2 storage capital and annualized control costs for the Stauffer plant would be in the range of \$570,000 and \$165,000, respectively, or about twice the cost for 95 percent control of the smaller storage control systems addressed in Table 3-17. Applying this annual cost and recovery credit for a 43 Mg/yr Option 2 emission reduction results in the following net cost and cost-effectiveness.

Total installed capital cost	<u>\$570,000</u>
Annualized cost	\$165,000
Recovery credit	<u>(20,100)</u>
Net annualized cost	144,900
Emission reduction	48 Mg; 95%
Cost-effectiveness	\$ 3,020/Mg

Loading control: Basic derivation of annualized and capital costs for loading controls is explained in 3.5.1. From Figure 3-3, July 1982 total annualized costs for 90 percent control of loading emissions at the carbon disulfide plant can be estimated at \$25,800. Assuming 65 percent of the total annualized cost as capital charges and an annualized capital cost factor of 0.20 results in an estimated capital cost of \$83,900. The following net cost and cost-effectiveness are based on an Option 2 emission reduction derived from Tables 5-2 and 5-5.

Total installed capital cost	<u>\$83,900</u>
Annualized cost	\$25,800
Recovery credit	<u>(5,900)</u>
Net annualized cost	19,900
Emission reduction	14 Mg/yr; 90%
Cost-effectiveness	\$ 1,420/Mg

Secondary controls: There were no secondary emissions identified for the carbon disulfide process.

Summary: Table 5-7 summarizes Option 2 control costs for the carbon disulfide plant. Process costs include estimates for the existing condenser cited under Option 1 as well as the Option 2 retrofit condenser.

TABLE 5-7. OPTION 2 CARBON DISULFIDE PLANT CONTROL COSTS

	Process	Fugitive	Storage	Loading	Total
<u>Plant 2</u>					
Capital cost (\$)	242,500	30,700	570,000	83,900	927,100
Annual cost (\$/yr)	(2,856,000)	10,000	144,900	19,900	(2,681,200)

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## 6.0 CHLOROFLUOROCARBON PRODUCTION FROM CARBON TETRACHLORIDE FEEDSTOCK

This chapter discusses the chlorofluorocarbon (CFC) industry and its associated carbon tetrachloride emissions. Section 6.1 presents a brief description of the production process for chlorofluorocarbons 11 and 12 and related emissions. Section 6.2 develops estimates of uncontrolled carbon tetrachloride emissions for existing CFC plants. Section 6.3 discusses existing controls and regulations for this industry, the resulting level of Option 1 control, and associated carbon tetrachloride emissions. Section 6.4 presents a discussion of estimated best controls (Option 2) and Section 6.5 discusses the costs of applying these options.

### 6.1 CHLOROFLUOROCARBON 11/12 PROCESS DESCRIPTION

#### 6.1.1 General Information

About 90 percent of domestic carbon tetrachloride use is as a feedstock for production of dichlorodifluoromethane (CFC 12) and trichlorofluoromethane (CFC 11).<sup>1</sup> Chlorofluorocarbons 11 and 12 generally are produced at facilities which also have the capacity to produce a number of other chlorofluorocarbons. Information on the product mixes of individual CFC plants is not available in the literature.

A list of CFC production facilities, their locations, and total production capacities (for all CFC) is presented in Table 6-1. It has been reported that the DuPont plants at Louisville, Kentucky and Corpus Christi, Texas and the Allied plants at Elizabeth, New Jersey and Baton Rouge, Louisiana do not currently make CFC 11 or 12. The Louisville and Elizabeth plants produce CFC 22, while the Corpus Christi and Baton Rouge plants produce CFC 113 and 114.<sup>2,3,4,5</sup> One reference does cite a breakdown of a total 1981 chlorofluorocarbon production of 435,000 Mg, as follows: CFC 12 -- 147,000 Mg; CFC 11 -- 74,000 Mg; CFC 22 -- 114,000 Mg, and others (113, 114, 115) -- 100,000 Mg.<sup>6</sup>

TABLE 6-1. CHLOROFLUOROCARBON PRODUCERS

Plant number	Company	Location	CFC production capacity (Mg) <sup>9</sup>
-	Allied	Elizabeth, NJ	a,b
1	DuPont	Deepwater, NJ	c
2	Pennwalt	Calvert City, KY	36,000
-	DuPont	Louisville, KY	b,c
3	Allied	Danville, IL	a
4	DuPont	Montague, MI	c
5	Kaiser Aluminum and Chemical	Gramercy, LA	30,000
-	Allied	Baton Rouge, LA	a,b
-	DuPont	Ingleside, TX	b,c
6	Essex Chemical Corp./Racon	Wichita, KS	20,000
7	DuPont	Antioch, CA	c
8	Allied	El Segundo, CA	a

<sup>a</sup>Total Allied capacity is estimated at 181,000 Mg, which includes capacity idled at Elizabeth, NJ and Baton Rouge, LA.<sup>9</sup>

<sup>b</sup>Allied plants at Elizabeth, NJ and Baton Rouge, LA and the DuPont plants at Louisville, KY and Ingleside, TX do not produce CFC-11 or CFC-12.2,3,4,5

<sup>c</sup>Total DuPont capacity is estimated at 227,000 Mg.<sup>9</sup>

### 6.1.2 Process Description

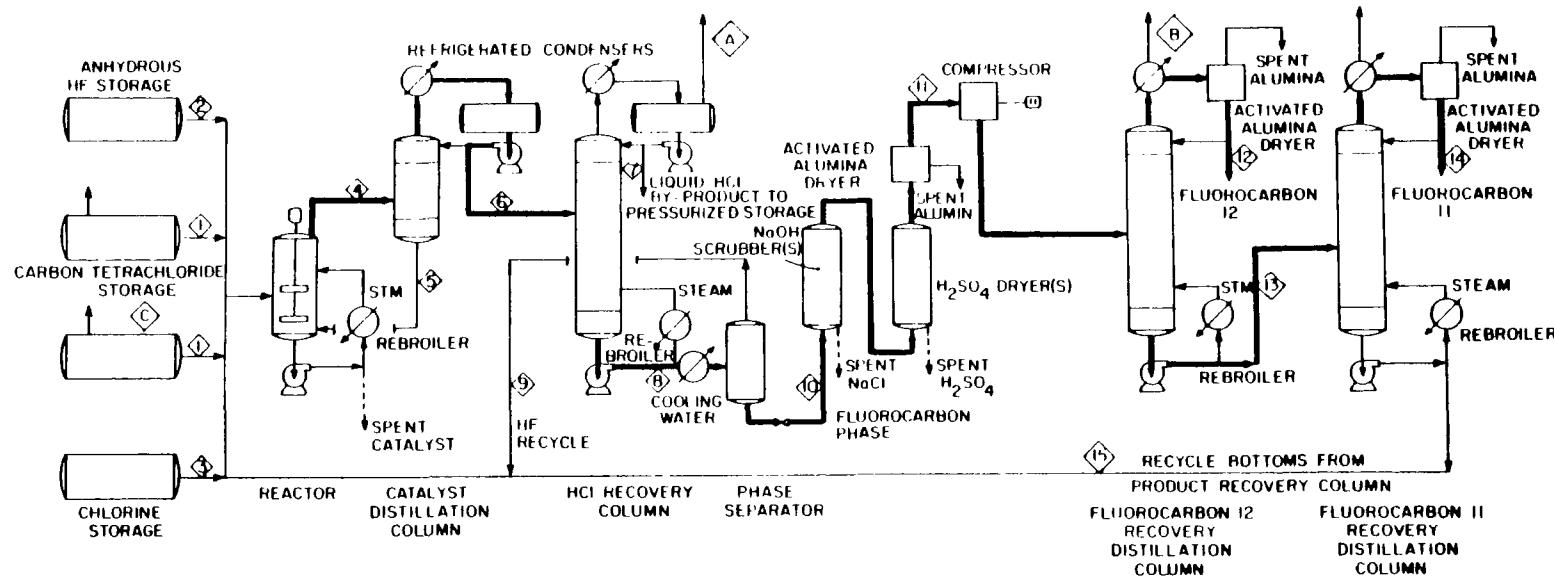
To produce CFC 11 and 12, carbon tetrachloride, anhydrous hydrogen fluoride and chlorine are reacted in liquid phase in the presence of antimony pentachloride catalyst at temperatures from 0 to 200°C and pressures of 100 to 3,400 kPa.<sup>7,8</sup> Further process steps remove catalyst entrained in the product stream, recover HCl and HF, scrub and dry the product stream, and recover chlorofluorocarbons by distillation. A typical process flow diagram is shown in Figure 6-1. A number of process variations are possible, and some of the above steps are not used at older plants.<sup>7</sup>

### 6.1.3 Carbon Tetrachloride Emission Factors for Chlorofluorocarbon Production

Uncontrolled emission factors for the CFC 11 and 12 production processes are presented in Table 6-2. One source of carbon tetrachloride process emissions is venting of the reactor through the HCl recovery column (Vent A in Figure 6-1). This vent purges noncondensibles and small amounts of inert gases which enter the reactor with the chlorine feed stream. The vent stream is not reported to contain carbon tetrachloride during typical process operation. However, during mechanical maintenance operations, the fluorination reactor is vented through the HCl column accumulator and at these times the vent stream contains carbon tetrachloride.

The emission point indicated by "B" in Figure 6-1 is a distillation column purge vent that was reported for the Allied plant at Danville, Illinois. Emissions from this vent at other plants do not contain any carbon tetrachloride, but the Danville plant recovers potential CFC 12 losses at this vent with a refrigerated condenser and a scrubber using carbon tetrachloride feedstock.<sup>12</sup> Emissions from this scrubber have been estimated at 0.171 kg/hr of carbon tetrachloride at a production rate of 7,576 kg/hr, which is equivalent to an emission factor of 0.023 kg carbon tetrachloride per Mg of CFC production.<sup>13</sup>

Fugitive emissions can result from leaks in process valves, pumps, compressors and pressure relief valves. Uncontrolled storage emissions result from the storage of carbon tetrachloride feedstock in fixed roof tanks. No secondary emissions of carbon tetrachloride have been reported.



NOTE: Letters in this figure refer to process vents described in the text and tables. Numbers refer to process descriptions in the first reference cited below. Heavy lines indicate final product streams throughout the process.

Figure 6-1. Process flow diagram for chlorofluorocarbon production.<sup>7,10</sup>

TABLE 6-2. UNCONTROLLED CARBON TETRACHLORIDE EMISSION FACTORS FOR CHLOROFLUOROCARBON 11 AND 12 PRODUCTION

Emission source	Source designation <sup>a</sup>	Uncontrolled carbon tetrachloride emission factor <sup>b</sup>
Reactor venting	A	0.042 kg/Mg <sup>11</sup>
Distillation column <sup>c</sup>	B	0.023 kg/Mg <sup>13</sup>
Fugitive		0.18 kg/Mg <sup>10</sup>
Storage	C	0.19 kg/Mg <sup>14</sup>

<sup>a</sup>Refers to process vents shown in Figure 6-1.

<sup>b</sup>Emission factors in terms of kg/Mg refer to kg of carbon tetrachloride emitted per Mg of production of CFC 11 and 12.

<sup>c</sup>The Allied plant at Danville, Illinois reports emissions from a scrubber that uses carbon tetrachloride to recover CFC 12 losses from a distillation column purge vent.<sup>12</sup>

## 6.2 UNCONTROLLED CHLOROFLUOROCARBON PLANT EMISSIONS

A number of preliminary steps were required to allow estimation of uncontrolled carbon tetrachloride emissions from individual CFC 11/12 production facilities, and also to facilitate later estimates of controlled emissions and control costs for Options 1 and 2. These include use of model plants, apportionment of CFC production capacity to specific plants, and development of an industry-wide capacity utilization rate. These steps are discussed below. Uncontrolled emissions are then estimated.

### 6.2.1 Model Plants

Emissions and control cost estimates for the production of CFC 11 and 12 are based on a representative model plant. This model plant was chosen to be the same as that used in previous investigations of CFC 11 and 12 production processes.<sup>10,14</sup> A flow diagram for the model plant is shown in Figure 6-1. The total annual production capacity of the model plant producing CFC 11 and 12 is 66,400 Mg, based on 8,760 hours per year of operation. It should be noted that use of model plant parameters does not allow consideration of variations between different CFC 11 and 12 production facilities. Several processes have been reported to vary from the model plant in ways that may affect the accuracy of emission and control cost estimates. These differences are discussed in more detail in 6.3.1.

### 6.2.2 Capacity Apportionment

To derive plant-by-plant emissions and costs from model plant data, it was necessary to apportion the known total capacity of these plants to the individual CFC 11 and 12 processes. Plant-specific CFC production data were only available for three plants, as shown in Table 6-1. For the Allied plant at El Segundo, California, 2,100 Mg of CFC 11/12 were reportedly produced in 1981.<sup>5</sup> Applying the industry-wide CFC capacity utilization factor of 88 percent (see 6.2.4) results in an estimated plant capacity of 2,400 Mg. Since individual plant capacities for other CFC 11/12 production facilities were not reported, apportionment was based on the percentage of industry-wide CFC production devoted to CFC 11 and 12, estimated to be 50.8 percent in 1981.<sup>6</sup> This percentage was

multiplied by the available total CFC capacities of each producer (Table 6-1) to derive an estimate of CFC 11 and 12 capacity for each producer.

The capacity of the Allied plant at Danville, Illinois (Plant 3; 89,500 Mg/yr) was estimated by subtracting the estimated Allied/EI Segundo (Plant 8) capacity of 2,400 Mg/yr from the estimated Allied total capacity of 91,900 Mg/yr. The capacities of the three active DuPont CFC 11/12 plants were estimated at 38,400 Mg/yr each by assuming equal distribution of the estimated 115,300 Mg/yr company CFC 11/12 capacity. Estimated capacity apportionment for the individual plants is presented in Table 6-3. In 1981, the ratio of nationwide CFC 11 production to that of CFC 12 was 1:2.<sup>6</sup>

TABLE 6-3. CAPACITY APPORTIONMENT FOR CFC 11/12 PLANTS

Plant	Estimated CFC 11/12 capacity (Mg)
1	38,400
2	18,300
3	89,500
4	38,400
5	15,200
6	10,200
7	38,400
8	2,400
Total	250,800

#### 6.2.3 Proportionality and Scales of Production

Throughout the analysis, direct proportionality of emissions, control efficiencies and costs over all scales of production was assumed. The plant capacity factors in Table 6-4, derived by dividing each plant's assumed CFC 11/12 production capacity (Table 6-3) by that of the model

plant (66,400 Mg/yr), were used to apply model plant emission estimates and control costs to each plant.

TABLE 6-4. CFC PLANT CAPACITY FACTORS (RELATIVE TO MODEL PLANT)

Plant	CFC 11/12 factor
1	0.58
2	0.28
3	1.35
4	0.58
5	0.23
6	0.15
7	0.58
8	0.04
Total	3.79

#### 6.2.4 Capacity Utilization

Based on the 1981 total chlorofluorocarbon production of 435,000 Mg<sup>6</sup>, and the corresponding domestic production capacity of 494,000 Mg<sup>9</sup>, a uniform capacity utilization rate of 0.88 was applied to all plants in estimation of emissions and also to the model plant emission reductions used in cost estimates.

#### 6.2.5 Uncontrolled Emissions

Uncontrolled carbon tetrachloride emissions for the CFC 11/12 model plant (Table 6-5) were based on the model plant capacity of 66,400 Mg/yr and the uncontrolled emission factors from Table 6-2. The industry-wide capacity utilization of 0.88 and the plant capacity factors shown in Table 6-4 were applied to the model plant emission estimates to produce the plant-specific uncontrolled emission estimates presented in Table 6-6. Process emissions for the Allied plant at Danville, Illinois (Plant 3)

include emissions from reactor venting as well as the scrubber which uses carbon tetrachloride to recover CFC 11 losses from the distillation column purge vent.<sup>12</sup> Process emissions from all other plants are from reactor venting. No uncontrolled storage emissions were listed for the Essex plant at Wichita, Kansas (Plant 6) because there is no storage of carbon tetrachloride on site. Carbon tetrachloride is piped directly from the adjacent Vulcan carbon tetrachloride production facility.<sup>16</sup>

TABLE 6-5. UNCONTROLLED CFC 11/12 MODEL PLANT CARBON TETRACHLORIDE EMISSIONS

Source	Model plant emissions (Mg/yr)
Reactor venting	2.79
Distillation column	1.53 <sup>a</sup>
Fugitive	12.0
Storage	12.6 <sup>b</sup>
Total	28.9

<sup>a</sup>Only at Allied/Danville, IL (Plant 3).

<sup>b</sup>Does not apply at Essex/Wichita, KS (Plant 6).

TABLE 6-6. UNCONTROLLED CARBON TETRACHLORIDE EMISSIONS FROM CFC 11/12 PRODUCTION FACILITIES

Plant	Uncontrolled emission estimates (Mg/yr)			Total
	Process	Fugitive	Storage	
1	1.42	6.12	6.43	13.97
2	0.69	2.96	3.10	6.75
3	5.13	14.26	14.97	34.36
4	1.42	6.12	6.43	13.97
5	0.56	2.43	2.55	5.54
6	0.37	1.58	0 <sup>a</sup>	1.95
7	1.42	6.12	6.43	13.97
8	0.09	0.38	0.40	0.87
Total	11.10	39.97	40.31	91.38

<sup>a</sup>No storage at Plant 6.

## 6.3 OPTION 1 CONTROLS AND EMISSIONS FOR CHLOROFLUOROCARBON PRODUCTION

Option 1 emission controls relating to the production of CFC 11 and 12 are discussed in this section. These include existing controls at individual plants, currently applicable State regulations, and Group III CTG controls which will be required in ozone NAAQS nonattainment areas requesting extensions beyond 1982.

### 6.3.1 Existing Controls

Information on control technology currently in place at CFC 11/12 production facilities was obtained in telephone conversations with State agency personnel and from previous EPA surveys. No existing controls were identified for carbon tetrachloride emissions from the venting of the reactor through the HCl recovery column during maintenance (emission point "A" in Figure 6-1), or for the carbon tetrachloride emissions induced by use of a carbon tetrachloride scrubber to control CFC 12 emissions from the first distillation column of the Allied plant at Danville, Illinois (Plant 3).

Storage of carbon tetrachloride is in fixed roof tanks with no controls at all of the CFC 11/12 production facilities except the DuPont plants at Deepwater, New Jersey (Plant 1) and Montague, Michigan (Plant 4) and the Essex/Racon plant at Wichita, Kansas (Plant 6) as shown in Table 6-7. The Deepwater plant uses a floating roof tank for storage of carbon tetrachloride<sup>11</sup> and the Montague plant uses vapor balance during unloading of carbon tetrachloride into a fixed roof tank.<sup>15</sup> Storage of carbon tetrachloride at the Wichita plant is not required because it is obtained directly through a pipeline from storage tanks at the adjacent Vulcan carbon tetrachloride production facility.<sup>16</sup>

TABLE 6-7. EXISTING CARBON TETRACHLORIDE STORAGE CONTROLS AT CFC 11/12 PRODUCTION PLANTS

Plant number	Control device	Control efficiency	Reference
1	Floating roof	88	11, 17
2	No control	--	18
3	No control	--	12
4	Vapor balance	77 <sup>a</sup>	15, 19
5	No control	--	20
6	No on-site storage	--	16
7	No control	--	21
8	No control	--	22

<sup>a</sup>Based on a 90 percent control<sup>19</sup> of working losses from a fixed roof tank. Working losses were estimated as 86 percent of total losses from carbon tetrachloride storage as discussed in Appendix A-6.

No controls other than normal inspection and maintenance procedures were identified as currently being used by any plants to control fugitive emissions.

### 6.3.2 State Regulations

State regulations pertaining to CFC 11/12 production plants are presented in Table 6-8. Control efficiencies presented in the table are discussed in 2.2.1.

Carbon tetrachloride is not included in the "VOC" definition for VOC storage and fugitive VOC in Louisiana. Also, it is not included in the "organic liquid" definition which is applied to VOC storage in the San Francisco Bay Area (California). However, for purposes of this source assessment, it has been assumed that the Louisiana and Bay Area SIP provisions cited for the Kaiser plant at Gramercy, Louisiana (Plant 5) and the DuPont plant at Antioch, California (Plant 7), will be enforceable for carbon tetrachloride despite the current State definitions. This is because the Bay Area definition will probably be changed to conform with the VOC definition in the VOL storage CTG when this CTG is adopted there, and because Louisiana is currently applying its VOC regulations to carbon tetrachloride sources.<sup>4</sup> The New Jersey toxics regulation, which requires control of carbon tetrachloride emissions "of a rate equivalent to advances in the art of control", was assumed to be equivalent to the estimated best controls discussed in 6.4.1. These controls will provide 95 percent control of storage emissions and 56 percent control of fugitive emissions, but effective controls do not appear to be available for the maintenance-related process emissions from CFC 11/12 production.

The carbon tetrachloride storage tank at the Allied plant at El Segundo (Plant 8) is under the 39,630 gallon exemption level of South Coast Air Quality Management District Rule 463, so no State control requirement was assumed for storage emissions there.<sup>21</sup>

TABLE 6-8. CURRENT STATE REGULATIONS APPLYING TO CARBON TETRACHLORIDE EMISSIONS FROM CFC 11/12 PRODUCTION FACILITIES

Plant number	State	Applicable State regulations <sup>a</sup>	Control efficiency (%) <sup>b</sup>
1	New Jersey	<u>VOC Storage:</u> Carbon tetrachloride tanks over 300,000 gallons must be equipped with an external or internal floating roof with at least one tight seal.  <u>Toxics:</u> New Jersey toxic substances rules require registration of carbon tetrachloride emissions and control "at a rate or concentration equivalent to advances in the art of control" for the type of emission involved.	95
2	Kentucky	None (regulations only cover petroleum liquids and/or gasoline).	--
3	Illinois	<u>VOC Storage:</u> Tanks over 40,000 gallons must be a pressure tank or be equipped with a floating roof, a vapor recovery system capable of 85 percent collection which includes a disposal system, or equipment or means of equal efficiency.  <u>VOC Fugitive:</u> No pump or compressor may discharge over 2 cubic inches of liquid VOC in any 15-minute period.	85
4	Michigan	<u>VOC Storage:</u> Tanks over 40,000 gallons must be pressure tanks or have either a floating roof, vapor recovery system, or equivalent with 90 percent control.	90
5	Louisiana	<u>VOC Storage:</u> Tanks over 40,000 gallons which are not pressure tanks must have submerged fill and either (a) floating roof, (b) a vapor loss control system equivalent to floating roof, or (c) other equivalent equipment or means. Tanks from 250 to 40,000 gallons must have submerged fill or vapor recovery or other equivalent equipment or means.	95

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CONTINUED

TABLE 6-8. (continued)

Plant number	State	Applicable State regulations <sup>a</sup>	Control efficiency (%) <sup>b</sup>
5 (con't)		<u>VOC Fugitives:</u> Pumps and compressors must be equipped with mechanical seals, or equivalent equipment or means. Best practical housekeeping and maintenance practices are also required.	0
6	Kansas	None.	--
7	California (Bay Area)	<u>VOC Storage:</u> Organic liquid storage tanks between 260 and 40,000 gallons must have submerged fill or equivalent. Tanks over 40,000 gallons must have floating roof, vapor recovery with 95 percent efficiency or other control with 95 percent efficiency.	95
		<u>Valves and Flanges:</u> Annual inspection and repair or minimization of leaks in chemical plant complexes.	0
8	California (South Coast)	<u>VOC Storage:</u> Tanks over 39,630 gallons must be pressure tanks or be equipped with one of the following: (a) external floating roof, (b) fixed roof with internal-floating-type cover, (c) 95 percent vapor recovery system, or (d) other equipment with 95 percent control efficiency.  <u>Pumps and Compressors:</u> Seals or other devices of equal efficiency are required and must be maintained to prevent: (a) leakage of more than 3 drops/minute, (b) visible liquid mist or vapor, and (c) any visible indication of leakage at or near the shaft/seal interface of gas compressors.  <u>Valves and Flanges:</u> Annual inspection, repair and re-inspection are required, as well as seals on open-ended lines.	95 <sup>d</sup> 42

6-14

CONTINUED

TABLE 6-8. (continued)

Plant number	State	Applicable State regulations <sup>a</sup>	Control efficiency (%) <sup>b</sup>
8 (con't)		<u>Safety Relief Valves:</u> Must be vented to a vapor recovery/disposal system, protected by a rupture disk or maintained by an approved inspection system.	

<sup>a</sup>Refer to 2.2.1 for references to State regulations.

<sup>b</sup>Refer to 2.2.1 for discussion of control efficiency estimates.

<sup>c</sup>Assumed to be equivalent to estimated best controls which have a control efficiency of 95 percent for storage emissions and 56 percent for fugitive emissions.

<sup>d</sup>Storage at Plant 8 is below the 39,630 gallon cutoff in Rule 463.

### 6.3.3 Group III Control Techniques Guidelines

Since it is anticipated that ozone nonattainment areas which have received extensions beyond 1982 will be required to adopt all Group III CTGs, these CTGs were reviewed for applicability to known sources of carbon tetrachloride at CFC 11/12 production facilities. Two Group III CTGs (covering volatile organic liquid storage and fugitive emissions from synthetic organic chemical, polymer and resin manufacturing) would apply to operations in post-1982 attainment-date areas which store carbon tetrachloride or produce chlorofluorocarbons 11 or 12. Table 6-9 presents ozone NAAQS nonattainment status for CFC 11/12 production plants. As shown in the table, only Plants 1, 7, and 8 (DuPont at Deepwater and Antioch and Allied at El Segundo, respectively) are currently anticipated to be subject to these CTGs. As discussed in 2.2.2, these CTGs are expected to result in 95 percent of storage emissions and 42 percent control of fugitive emissions at affected plants.

TABLE 6-9. OZONE NATIONAL AMBIENT AIR QUALITY STANDARD ATTAINMENT STATUS FOR CFC 11/12 PLANTS<sup>23,24</sup>

Plant	Ozone NAAQS attainment status	Post-1982 attainment date granted?
1	Nonattainment	Yes
2	Nonattainment	No
3	Nonattainment	No
4	Nonattainment	No
5	Nonattainment	No
6	Attainment	--
7	Nonattainment	Yes
8	Nonattainment	Yes

#### 6.3.4 Combined Option 1 Controls

Control efficiencies for the Option 1 controls applicable to carbon tetrachloride emissions from CFC 11/12 production plants are summarized in Table 6-10. Each efficiency represents the most stringent of existing, State-required or Group III CTG controls as discussed above.

TABLE 6-10. OPTION 1 CONTROL SUMMARY FOR CFC 11/12 PRODUCTION PLANTS

Plant number	Option 1 control efficiency (percent)		
	Process	Fugitive	Storage
1	--	56	95
2	--	--	--
3	--	--	85
4	--	--	90
5	--	--	95
6	--	--	--
7	--	42	95
8	--	42	95

#### 6.3.5 Estimated Option 1 Emissions

Table 6-11 summarizes annual emissions from CFC 11/12 production plants which would result from the use of the Option 1 controls. These emission estimates were derived by applying the Option 1 control efficiencies in Table 6-10 to uncontrolled carbon tetrachloride emission rates in Table 6-6.

TABLE 6-11. OPTION 1 CONTROLLED EMISSIONS FOR CFC 11/12 PRODUCTION PLANTS

Plant number	Process	Option 1 controlled emissions (Mg/yr)		
		Fugitive	Storage	Total
1	1.42	2.69	0.32	4.43
2	0.69	2.96	3.10	6.75
3	5.13	14.26	2.25	21.64
4	1.42	6.12	0.64	8.18
5	0.56	2.43	0.13	3.12
6	0.37	1.58	0	1.95
7	1.42	3.55	0.32	5.29
8	0.09	0.22	0.02	0.33
Total	11.10	33.81	6.78	51.69
Option 1 control efficiency (%)	--	15	83	43

## 6.4 OPTION 2 CONTROLS AND EMISSIONS FOR CHLOROFLUOROCARBON PRODUCTION

### 6.4.1 Estimated Best Controls

The following control methods were selected as potentially applicable control technology for carbon tetrachloride emissions from CFC 11/12 production. No feasible controls were identified for emissions which occur as a result of venting of the reactor during mechanical maintenance operations. This is due to the intermittent and fugitive nature of these emissions. Also, no feasible controls were identified for emissions from the existing scrubber at the Allied/Danville plant which uses carbon tetrachloride to recover CFC 12 from a distillation column.

Fugitive emissions can be controlled with a quarterly inspection and repair program similar to the Group III CTG at efficiencies up to 42 percent, but it was estimated that monthly inspections and equipment specifications can raise this to about 56 percent.<sup>25</sup> Emissions from storage of carbon tetrachloride can be controlled with vapor recovery and -20<sup>0</sup>C refrigerated condensation systems, at efficiencies up to 95 percent.<sup>26,27,28</sup>

### 6.4.2 Estimated Option 2 Emissions

Table 6-12 summarizes annual carbon tetrachloride emissions and control efficiencies which can be achieved by CFC 11/12 production plants with the Option 2 controls described in 6.4.1.

TABLE 6-12. OPTION 2 CONTROLLED EMISSIONS FOR CFC 11/12 PRODUCTION PLANTS

Plant number	Process	Option 2 controlled emissions (Mg/yr)			Total
		Fugitive	Storage		
1	1.42	2.69	0.32		4.43
2	0.69	1.30	0.16		2.15
3	5.13	6.27	0.75		12.15
4	1.42	2.69	0.32		4.43
5	0.56	1.07	0.13		1.76
6	0.37	0.70	0		1.07
7	1.42	2.69	0.32		4.43
8	0.09	0.17	0.02		0.28
Total	11.10	17.58	2.02		30.70
Option 2 control efficiency (%)	0	56	95		66

## 6.5 CONTROL COSTS FOR CHLOROFLUOROCARBON PLANTS

This section presents control cost estimates for the Option 1 and Option 2 controls discussed in this chapter. Model plant control costs are developed for storage and fugitive controls, and plant-specific control costs for Options 1 and 2 are presented under Summary headings at the end of 6.5.1 and 6.5.2. As discussed in Sections 6.3 and 6.4, no process controls were identified, and loading and secondary emissions of carbon tetrachloride do not occur at CFC plants. Costing methodology and assumptions are discussed further in Chapter 1. All costs are for July 1982.

### 6.5.1 Option 1 Control Costs

This section provides cost estimates for the Option 1 CFC plant controls discussed in 6.3.4.

Fugitive control: Option 1 fugitive emission controls include 42 percent control at Plants 8 and 9 and 56 percent control at Plant 1. The available information on fugitive emission sources in carbon tetrachloride service at CFC plants consists of an overall count of 110 for Plant 8 and a breakdown for Plant 7 as follows: 28 valves, 52 flanges, and 5 quick-disconnect couplings, with a total of 90.<sup>21,22</sup> Since the breakdown for Plant 7 totals 85 units, it is likely that the remaining 5 units were pumps. These counts are much smaller than the totals for the small SOCMI fugitives model plant shown in Table 3-15. The SOCMI model plant also includes compressors and relief valves, while flanges are not included in the SOCMI fugitive CTG. Due to these differences, SOCMI model plant costs could not be used and the costs in the following paragraph for the CFC model plant were estimated. It was assumed that the relevant CFC model plant fugitive source inventory is equivalent to about 40 valves and 5 pumps, based on the breakdown and totals cited above (quick-disconnect couplings were assumed to be equivalent to two valves for costing purposes)

Costs of the monitoring instrument are the same for both Option 1 control efficiencies, and include a capital cost of \$11,900, annualized capital cost of \$2,744 and annual operating cost of \$4,256.<sup>29</sup> Capital costs for initial leak detection and repair of pumps and valves under either control program are about \$40 per pump and \$2.80 per valve, with

annualized capital costs of \$8.75 per pump and \$0.50 per valve.<sup>30</sup> Annual costs for monthly inspection and repair (56 percent control) are \$330 per pump and about \$19 per valve.<sup>30</sup> To estimate annual costs for a quarterly inspection and repair program (42 percent control), the cost of monitoring labor hours for a monthly program was reduced by 75 percent. Assuming no change in repair labor hours, costs of \$280 per pump and \$9.50 per valve were estimated for the quarterly program.<sup>31</sup> These unit costs for 40 valves and 5 pumps result in the following model plant costs.

	<u>42 percent control</u>	<u>56 percent control</u>
<u>Capital costs</u>		
Monitoring instrument	\$ 11,900	\$ 11,900
Pumps	200	200
Valves	<u>112</u>	<u>112</u>
Total	\$ 12,212	\$ 12,212

#### Annual operating and capital costs

Monitoring instrument	\$ 7,000	\$ 7,000
Pumps	1,444	1,695
Valves	<u>400</u>	<u>780</u>
Total	\$ 8,844	\$ 9,475

These costs and estimated model plant emission reductions at 0.88 percent capacity utilization result in the following net cost and cost-effectiveness analysis.

	<u>42 percent control</u>	<u>56 percent control</u>
Total installed capital cost	\$ <u>12,200</u>	\$ <u>12,200</u>
Annualized costs	8,800	9,500
Recovery credit	( <u>1,850</u> )	( <u>2,470</u> )
Net annualized cost	\$ 6,950	\$ 7,030
Emission reduction	4.4 Mg	5.9 Mg
Cost-effectiveness	\$ 1,580/Mg	\$ 1,191/Mg

Storage controls: Previous assessments of CFC plants did not include model plant data on carbon tetrachloride feedstock storage. Table 6-13 provides available data on storage and estimated production capacities at CFC 11/12 plants. The tank at Plant 8 (DuPont/Antioch, CA) is below the 39,360 gallon regulatory exemption level, but other data in the original reference indicate that it is at least 33,000 gallons ( $125 \text{ m}^3$ ).<sup>22</sup> At the plant where actual CFC 11/12 production capacity and carbon tetrachloride storage capacity estimates are available (Plant 8), production is about 10 times the storage capacity. Applying this factor to the model plant production capacity (66,400 Mg/yr), the model plant storage tank is estimated at 7,000 Mg ( $4,300 \text{ m}^3$ ).

TABLE 6-13. CARBON TETRACHLORIDE STORAGE AT CFC 11/12 PLANTS

Plant	( $\text{m}^3$ )	(gallons)	Main storage tank capacity (Mg)	Reference	CFC 11/12 production capacity (Mg) <sup>a</sup>
1	5280	1,394,000	8,364	37	38,400
2			Not available		18,300
3			Not available		89,500
4	$\approx 380$	$\approx 100,000$	$\approx 604$	32	38,400
5	950	250,000	1,510	33	15,200
6			No on-site storage	16	10,200
7	160	42,636	257	34	38,400
8	< 150	< 39,360	< 239	34	2,400

<sup>a</sup>From 6.2.2 and Table 6-3.

Available costs for SOCMi storage control by refrigerated condensers are for tanks from 150 to  $2,840 \text{ m}^3$ .<sup>35</sup> For the case most similar to this control requirement (Case 3), graphical projection of these costs to the range of  $4,300 \text{ m}^3$  results in annual costs between 2.7 and 2.8 times the costs for the  $660 \text{ m}^3$  tank presented in 3.5.1 and Figure 3-2. The annual control costs for Option 1 control levels in Table 6-14

were estimated by inflating costs taken from Figure 3-2 to July 1982 and then applying a factor of 2.75 to account for the difference in tank sizes. Capital costs were then estimated using the original 0.29 annualization factor, which includes maintenance, capital recovery and miscellaneous capital-related costs.<sup>36</sup>

TABLE 6-14. ESTIMATED CFC 11/12 MODEL PLANT COSTS FOR REFRIGERATED CONDENSER CONTROL OF CARBON TETRACHLORIDE FEEDSTOCK STORAGE

Control efficiency (percent)	Capital cost of complete condenser system	Annualized cost of complete condenser system
95	\$783,300	\$227,200
90	\$481,700	\$139,700
85	\$325,200	\$94,300

Combining the above control cost estimates with corresponding model plant emission reductions and the 0.88 capacity utilization factor produces the following net annualized cost and cost-effectiveness data.

	95 percent control	90 percent control	85 percent control
Total installed capital cost	<u>\$783,300</u>	<u>\$481,700</u>	<u>\$325,200</u>
Annualized cost	\$227,200	\$139,700	\$ 94,300
Recovery credit	(4,400)	(4,200)	(3,900)
Net annualized cost	\$222,800	\$135,500	\$ 90,400
Emission reduction	10.5 Mg	10.0 Mg	9.4 Mg
Cost-effectiveness	\$21,200/Mg	\$13,600/Mg	\$9,600/Mg

Summary: Table 6-15 summarizes Option 1 model plant control costs for CFC 11/12 plants developed in this section. Table 6-16 presents estimated capital and annualized control costs for each plant. These costs were calculated by multiplying model plant costs for the Option 1 control efficiencies indicated in Table 6-10 by the plant capacity factors in Table 6-4.

TABLE 6-15. OPTION 1 CFC 11/12 MODEL PLANT CONTROL COSTS

Control type	Control efficiency (%)	Capital cost (\$)	Net annual cost (\$/yr)
Fugitive	42	12,200	7,000
	56	12,200	7,000
Storage	85	325,200	90,400
	90	481,700	135,500
	95	783,300	222,800

### 6.5.2 Option 2 Control Costs

This section provides estimates for the Option 2 CFC production plant controls discussed in Section 6.4.

Fugitive controls: Model plant control costs for 56 percent control under Option 2 are identical to those for 56 percent control under Option 1 in 6.5.1. These costs are as follows:

Total installed capital costs	\$ <u>12,200</u>
Annualized costs	9,500
Recovery credit	( <u>2,470</u> )
Net annual cost	\$ 7,030
Emission reduction	5.9 Mg
Cost-effectiveness	\$ 1,191/Mg

TABLE 6-16. OPTION 1 CFC 11/12 PLANT CONTROL COSTS

Plant	Fugitive	Capital costs (\$)		Total
		Storage		
1	7,100	454,000		461,100
2	--	--		--
3	--	439,000		439,000
4	--	279,000		279,000
5	--	180,000		180,000
6	--	--		--
7	7,100	454,000		461,100
8	500	31,300		31,800
Total	14,700	1,837,300		1,852,000

Plant	Fugitive	Net annual costs (\$)		Total
		Storage		
1	4,100	129,000		133,100
2	--	--		--
3	--	122,000		122,000
4	--	78,600		78,600
5	--	51,200		51,200
6	--	--		--
7	4,100	129,000		133,100
8	300	8,900		9,200
Total	8,500	518,700		527,200

-- indicates no Option 1 control

Storage control: Model plant control costs for 95 percent control and/or Option 2 are identical to those for 95 percent control under Option 1, in 6.5.1. These costs are as follows:

Total installed capital cost	\$ <u>783,300</u>
Annualized cost	227,200
Recovery credit	<u>(4,400)</u>
Net annualized cost	\$ 222,800
Emission reduction	10.5 Mg
Cost-effectiveness	\$ 21,200/Mg

Summary: Table 6-17 summarizes Option 2 model plant control costs for CFC 11/12 plants developed in this section. Table 6-18 presents estimated capital and annualized control costs for each plant. These costs were calculated by multiplying model plant costs in Table 6-17 by the plant capacity factors in Table 6-4.

TABLE 6-17. OPTION 2 CFC 11/12 MODEL PLANT CONTROL COSTS

Control type	Control efficiency (%)	Capital cost (\$)	Net annual cost (\$/yr)
Fugitive	56	12,200	7,000
Storage	95	783,300	222,800

TABLE 6-18. OPTION 2 CFC 11/12 PLANT CONTROL COSTS

Plant	Fugitive	Capital costs (\$)		Total
		Storage		
1	7,100	454,000		461,100
2	3,400	219,000		222,400
3	16,500	1,057,000		1,073,500
4	7,100	454,000		461,100
5	2,800	180,000		182,800
6	1,800	117,000		118,800
7	7,100	454,000		461,100
8	500	31,000		31,500
Total	46,300	2,966,000		3,012,300

Plant	Fugitive	Net annual costs (\$/yr)		Total
		Storage		
1	4,060	129,000		133,060
2	1,960	62,000		63,960
3	9,450	301,000		310,450
4	4,060	129,000		133,060
5	1,610	51,000		52,610
6	1,050	33,000		34,050
7	4,060	129,000		133,060
8	280	9,000		9,280
Total	26,530	843,000		869,530

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## 7.0 PROCESSES WITH CARBON TETRACHLORIDE BY-PRODUCT

Several organic chemical manufacturing process have been reported to result in the formation and emission of carbon tetrachloride. These processes, which are discussed individually in this chapter, include methanol hydrochlorination/methyl chloride chlorination, ethylene dichloride production, and production of trichloroethylene and perchloroethylene from ethylene dichloride.

Carbon tetrachloride emission sources at the plants addressed in this chapter may be subject to a number of regulations, including State regulations on process and fugitive emissions and the Group III SOCMI fugitive CTG discussed in Section 2.2. Storage and loading of carbon tetrachloride will not exceed the cut-off levels in State regulations and the VOL storage CTG. Detailed examination of the applicability and effects of these regulations was not possible within the scope of this project. Existing controls and other regulations which may apply are included in the sections below.

### 7.1 METHANOL HYDROCHLORINATION/METHYL CHLORIDE CHLORINATION

#### 7.1.1 Process Description

In this two-stage process, gaseous methanol typically is hydrochlorinated to produce methyl chloride, and methyl chloride is then chlorinated to produce methylene chloride and chloroform as principal products. Some plants produce methyl chloride by methane chlorination, and some methyl chloride producers do not use it as an intermediate in producing methylene chloride and chloroform. Carbon tetrachloride by-product is formed in the second step of the process. Here, methyl chloride is reacted with chlorine, forming a combination of hydrogen chloride, methylene chloride, chloroform, and a small amount of carbon tetrachloride. Further steps remove the hydrogen chloride and distill the principal products, leaving carbon tetrachloride and other heavier components as the final distillation

bottoms. In some cases, this crude carbon tetrachloride mixture is used onsite as a feedstock for a carbon tetrachloride/perchloroethylene chlorinolysis operation, but in other cases it is sold.<sup>1</sup>

Figure 7-1 is a typical process flow diagram for a combined methanol hydrochlorination/methyl chloride chlorination process. Table 7-1 lists plants which produce chloroform and methylene chloride by methyl chloride chlorination.

#### 7.1.2 Carbon Tetrachloride Emissions

Table 7-2 presents available emission factors for carbon tetrachloride from methyl chloride chlorination with source designations referring to Figure 7-1. These factors are based on a model plant assumed for previous EPA studies in which the carbon tetrachloride by-product was chosen to be 2 percent of a product mix which included 25 percent methyl chloride, 48 percent methylene chloride and 25 percent chloroform.<sup>7,8</sup> The emission factors for storage and handling are based on the assumption that the final distillation bottoms containing carbon tetrachloride are stored and then shipped off-site. Table 3-1 shows that the Dow and Vulcan plants have mixed hydrocarbon chlorinolysis production of carbon tetrachloride and perchloroethylene on-site.

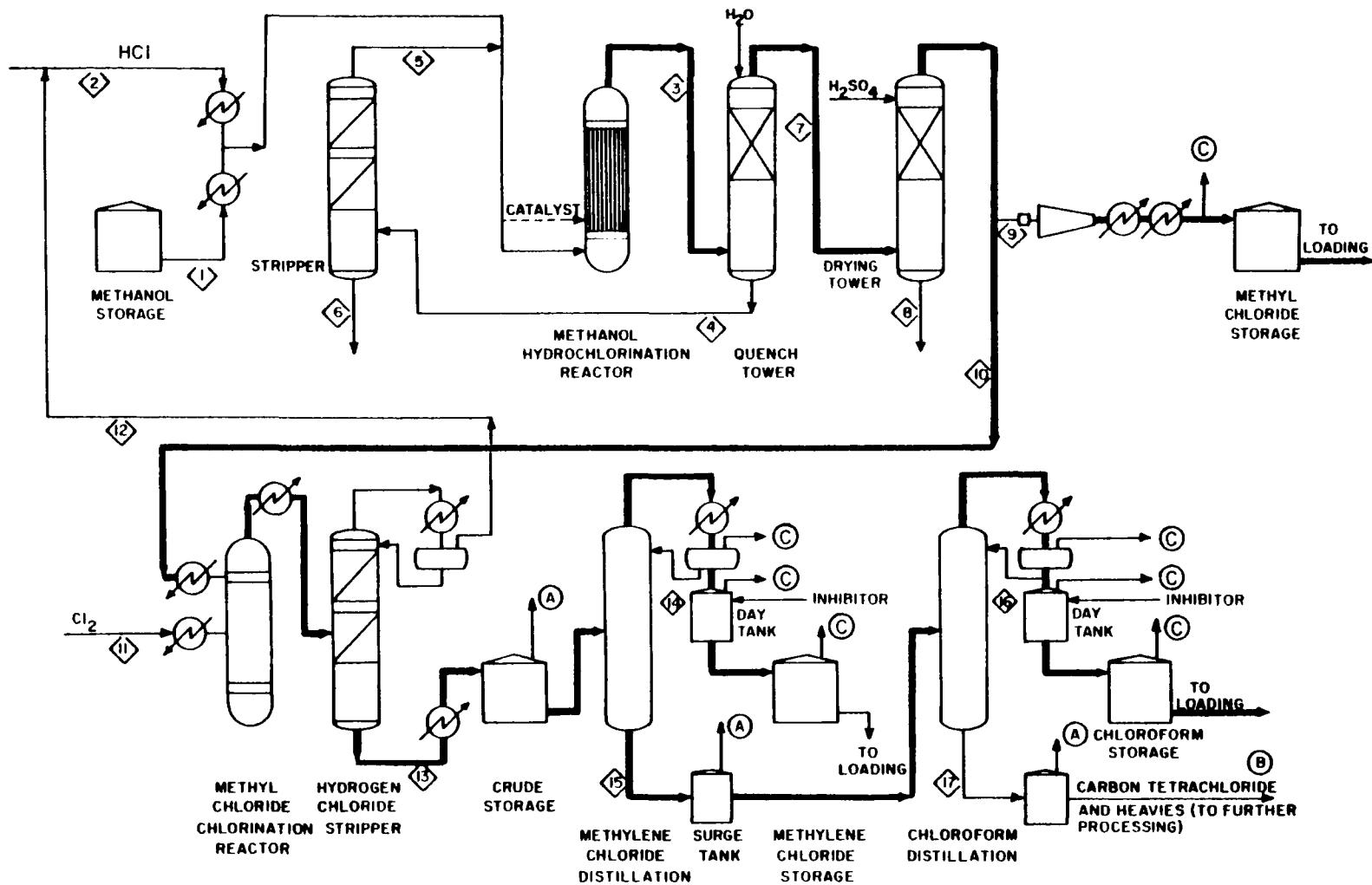
No information was found on existing emission controls for the sources of carbon tetrachloride listed in Table 7-2.

### 7.2 ETHYLENE DICHLORIDE PRODUCTION

#### 7.2.1 Process Description

Carbon tetrachloride is formed as a by-product during the production of ethylene dichloride (EDC). EDC can be produced from ethylene and chlorine by direct chlorination, and from ethylene and hydrogen chloride (HCl) by oxychlorination. These processes generally are used together, in what is known as the balanced process, wherever EDC and vinyl chloride monomer (VCM) are produced at the same facility. In VCM production, EDC is cracked to yield VCM and by-product HCl. In the balanced process, by-product HCl from VCM production is used in the oxychlorination process

7-3



NOTE: Letters in this figure refer to process vents described in the text and tables. Numbers refer to process descriptions in the first reference cited below. Heavy lines indicate final product streams throughout the process.

Figure 7-1. Process flow diagram for methanol hydrochlorination/methyl chloride chlorination process.<sup>1,2</sup>

TABLE 7-1. METHYLENE CHLORIDE AND CHLOROFORM PRODUCERS

EPA region	Company	Location	Annual capacity ( $\times 10^3$ Mg) <sup>3</sup>		Ozone NAAQS attainment status <sup>4,5</sup>	Post-1982 attainment date granted? <sup>4,5</sup>
			Chloroform	Methylene chloride		
III	Diamond Shamrock	Belle, WV	18	45	NA	No
	Linden Chemicals and Plastics	Moundsville, WV	14	23	A	--
IV	Stauffer Chemical Co.	Louisville, KY	34	27	NA	Yes
VI	Dow Chemical U.S.A.	Plaquemine, LA	45	86	NA	No
	Vulcan Materials Co.	Geismar, LA	28	36	NA	No
	Dow Chemical U.S.A.	Freeport, TX	45	93	NA	No
VII	Vulcan Materials Co.	Wichita, KS	50	59	A	--
			234	369		

A -- Attainment

NA -- Nonattainment

TABLE 7-2. UNCONTROLLED CARBON TETRACHLORIDE EMISSION FACTORS FOR  
METHANOL HYDROCHLORINATION/METHYL CHLORIDE CHLORINATION  
PROCESS

Emission source	Source designation <sup>a</sup>	Uncontrolled carbon tetrachloride emission factor <sup>b</sup>
Storage	A	0.15 kg/Mg
Handling <sup>c</sup>	B	0.52 kg/Mg
Process fugitive <sup>d</sup>		0.77 kg/hr

<sup>a</sup>Refers to process vents shown in Figure 7-1. Points labeled "C" have negligible carbon tetrachloride emissions.

<sup>b</sup>Emission factors in terms of kg/Mg refer to kg of carbon tetrachloride emitted per Mg of carbon tetrachloride produced, from Reference 6.

<sup>c</sup>Emission factor developed for cases in which impure by-product carbon tetrachloride is not transferred for further processing at hydrocarbon chlorinolysis co-facility.

<sup>d</sup>Fugitive emission rate is independent of process rate.

to produce about half of the EDC required for VCM production. The remaining EDC is produced by direct chlorination.<sup>9</sup> Table 7-3 lists EDC and VCM producers.

Assuming use of the balanced process at all plants producing VCM, which include about 87 percent of national EDC operating capacity, it follows that only 13 percent of the national EDC capacity is based on processes other than the balanced process. At these plants, EDC must be produced by direct chlorination of ethylene unless a supply of hydrogen chloride is available for oxychlorination. Adequate process and emissions data are available only for the balanced process, so the data presented here may not apply directly to the smaller plants which may use a single process. Most balanced process plants use air in the oxychlorination step, but three plants have been reported to use purified oxygen.<sup>11</sup> Figure 7-2 is a full process flow diagram for EDC production by the balanced air-based process; Figure 7-3 provides details for the oxychlorination step of the oxygen-based process.

#### 7.2.2 Carbon Tetrachloride Emissions

Table 7-4 gives estimated carbon tetrachloride emission factors for both variations of the oxychlorination step and other emission points common to the balanced process. Carbon tetrachloride process emissions for both oxychlorination process variations are based on VOC emission factors and vent gas composition data for the air-based process, which indicated a carbon tetrachloride composition of 1.4 percent of total VOC. Adjustments were made for differences in the proportion of chlorinated hydrocarbons in the VOC from the two process variations.<sup>17</sup>

For the direct chlorination process and column vents, the carbon tetrachloride emission factor is based on VOC emission factors, but direct estimates of carbon tetrachloride content are not available. Since an estimate of chloroform content was available, a factor was obtained by assuming that carbon tetrachloride and chloroform are present in the same proportions as in the oxychlorination process. Similarly, a light ends carbon tetrachloride content of 17 percent was used directly to obtain carbon tetrachloride factors from VOC emission

TABLE 7-3. ETHYLENE DICHLORIDE/VINYL CHLORIDE MONOMER PRODUCERS

EPA region	Company	Location	Annual capacity (x10 <sup>3</sup> Mg) <sup>3</sup>		Ozone NAAQS attainment status <sup>4,5</sup>	Post-1982 attainment date granted <sup>4,5</sup>
			EDC	VCM		
IV	B.F. Goodrich	Calvert City, KY	450	450	NA	No
VI	Borden, Inc.	Geismar, LA	230	280	NA	No
	Dow Chemical, U.S.A	Plaquemine, LA	860	565	NA	No
	E.I. duPont	Lake Charles, LA	525	320	NA	No
	Ethyl Corp.	Baton Rouge, LA	320	140	NA	No
	Formosa Plastics Corp.	Baton Rouge, LA	250	140	NA	No
	Georgia Pacific Corp.	Plaquemine, LA	750	450	NA	No
	B.F. Goodrich Co.	Convent, LA	360	--	NA	No
	PPG Industries, Inc.	Lake Charles, LA	1,225	410	NA	No
	Shell Chemical Co.	Norco, LA	545	320	NA	No
	Union Carbide Corp.	Taft, LA	70	--	NA	No
	Vulcan Materials Co.	Geismar, LA	160	--	NA	No
	Atlantic Richfield Co.	Port Arthur, TX	205	--	NA	No
	Dow Chemical U.S.A	Freeport, TX	725	70	NA	No
	Dow Chemical U.S.A	Oyster Creek, TX	475	340	NA	No
VII	Ethyl Corp.	Pasadena, TX	100	--	NA	Yes
	B.F. Goodrich Co.	Deer Park, TX	145	--	NA	Yes
	B.F. Goodrich Co.	La Porte, TX	720	450	NA	Yes
	Shell Chemical Co.	Deer Park, TX	635	380	NA	Yes
	Union Carbide Corp.	Texas City, TX	70	--	NA	No
			8,820	4,315		

Note: Stauffer Chemical Co. plant in Carson, CA was dismantled in 1982.<sup>10</sup>

NA -- Nonattainment

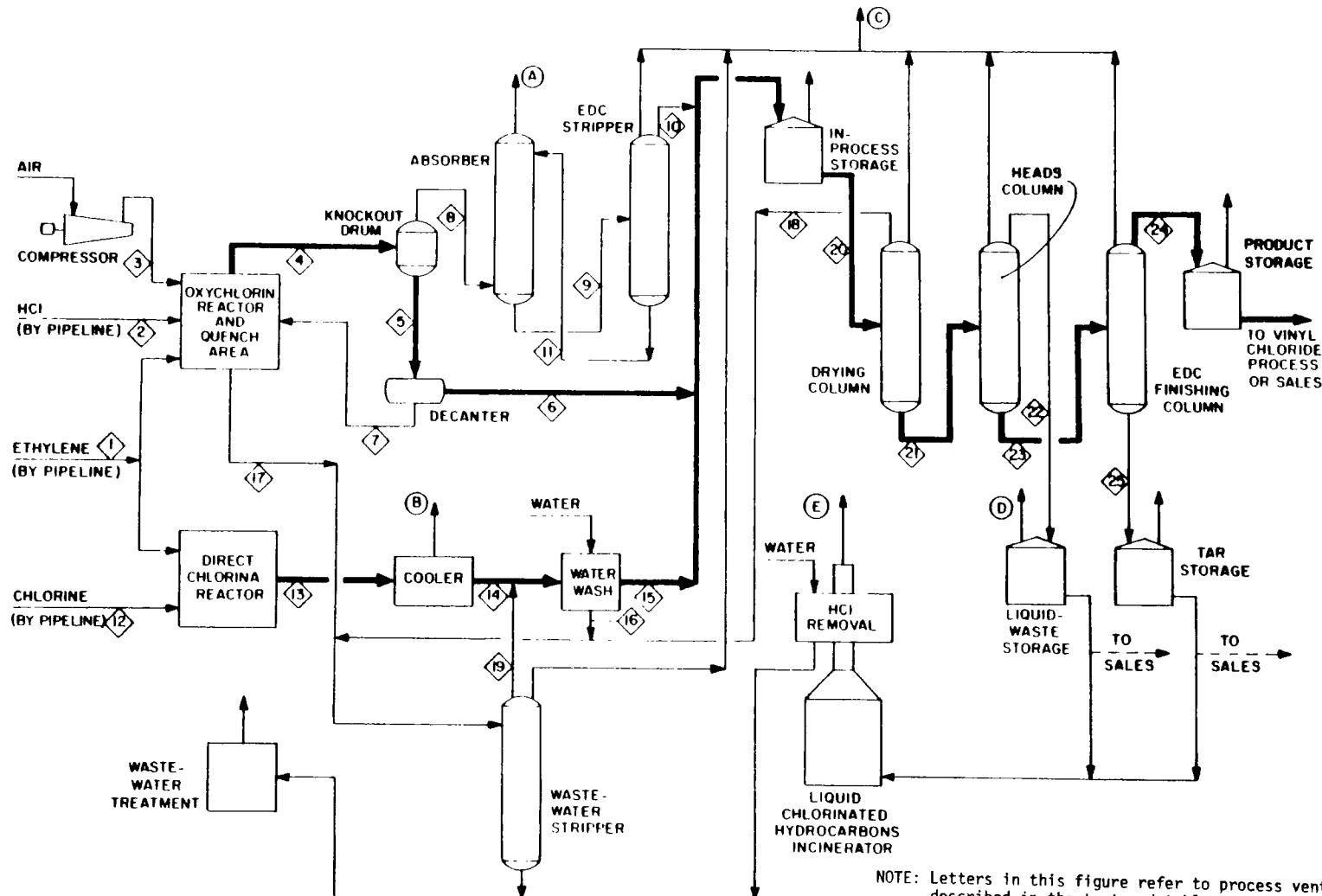
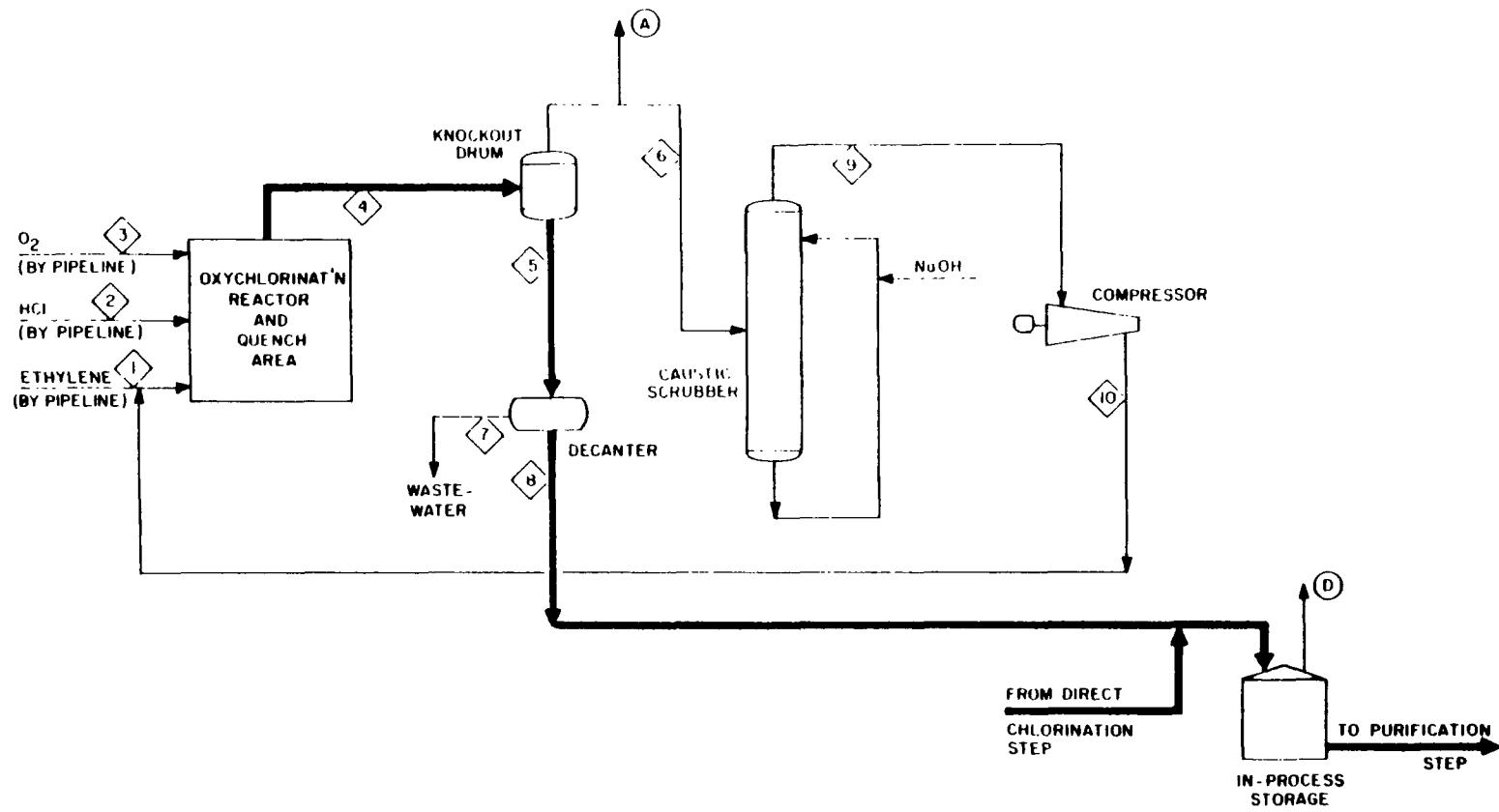


Figure 7-2. Process flow diagram for ethylene dichloride production by balanced air-based process. 12,13



NOTE: Letters in this figure refer to process vents described in the text and tables. Numbers refer to process descriptions in the first reference cited below. Heavy lines indicate final product streams throughout the process.

Figure 7-3. Process flow diagram for ethylene dichloride production by oxygen-based process, oxychlorination step.<sup>14,15</sup>

TABLE 7-4. UNCONTROLLED CARBON TETRACHLORIDE EMISSION FACTORS FOR ETHYLENE DICHLORIDE PRODUCTION BY THE BALANCED PROCESS

Emission source	Source designation <sup>a</sup>	Uncontrolled carbon tetrachloride emission factor <sup>b</sup>
Oxychlorination vent		
Air process	A	0.10 kg/Mg
Oxygen process	A	0.034 kg/Mg
Direct-chlorination vent	B	
Column vents	C	
Liquid waste storage	D	0.0050 kg/Mg
Incinerator	E	0.032 kg/Mg
Fugitive <sup>c</sup>		0.95 kg/hr

<sup>a</sup>Refers to process vents in Figure 7-2, except for the oxygen-based process oxychlorination vent which is shown in Figure 7-3. Unlabeled emission points have negligible carbon tetrachloride emissions.

<sup>b</sup>Emission factors in terms of kg/Mg refer to kg of carbon tetrachloride emitted per Mg of ethylene dichloride produced by both components of the balanced process, from Reference 16.

<sup>c</sup>Fugitive emission rate independent of process rate.

factors for liquid waste storage and incineration. A fugitive VOC emission rate was calculated assuming that fugitive emissions have the same composition as total process emissions (3.9 percent carbon tetrachloride).<sup>18</sup>

### 7.2.3 Emission Controls

Process emission controls used at ethylene dichloride plants include thermal and catalytic oxidization, solvent absorption, water scrubbing, refrigerated condensation and process-related control techniques.<sup>19</sup> Existing controls are summarized in Table 7-5. In addition, five plants in Louisiana currently using air-based oxychlorination have agreements with the State to convert to the oxygen-based process and to vent the emissions to a thermal oxidizer. These conversions are scheduled to be complete by the end of 1984, and include Conoco/Westlake, Ethyl/Baton Rouge, Formosa Plastics/Baton Rouge, Shell/Norco, and Vulcan/Geismar.<sup>30</sup>

The National Emission Standard (NESHAP) for vinyl chloride (40 CFR 61.62) includes the following limits for ethylene dichloride plants: Vinyl chloride must not exceed 10 ppm in exhaust gases from ethylene dichloride purification equipment, and emissions from oxychlorination reactors must not exceed 0.2 g/kg of ethylene dichloride product. The controls in Table 7-5 indicate that the principal method used for meeting these limits is thermal oxidation, which is estimated to have a VOC control efficiency of 98 percent or 20 ppm, whichever is less stringent.<sup>21</sup> Specific information is not available on carbon tetrachloride control efficiencies for the other controls cited in Table 7-5, and for process modifications, another potential control under the vinyl chloride NESHAP. In addition to State regulations and the SOCMi fugitive CTG, the Group III CTG for air oxidation processes described in 2.2.2 will also apply to a number of these plants, depending on the process used and NAAQS attainment status (see Table 7-3). Further investigation of the effectiveness of these controls for carbon tetrachloride was beyond the scope of this study.

## 7.3 PERCHLOROETHYLENE AND TRICHLOROETHYLENE PRODUCTION FROM ETHYLENE DICHLORIDE

### 7.3.1 Process Description

Carbon tetrachloride is formed as a by-product in the chlorination or oxychlorination of ethylene dichloride to produce perchloroethylene and trichloroethylene. Other chlorinated hydrocarbons may also be used

TABLE 7-5. EMISSION CONTROLS USED BY THE ETHYLENE DICHLORIDE INDUSTRY<sup>20</sup>

Company and location	Process used	Emission sources	Control technique or device used
Allied Baton Rouge, LA	Air	Oxychlorination vent Stripper ejector Purification vent	None None Return to process
Borden Geismar, LA	Air	Oxychlorination vent Direct-chlorination vent Purification vents	Thermal oxidizer Thermal oxidizer Thermal oxidizer
Conoco Westlake, LA	Air	Oxychlorination vent Direct-chlorination vent Purification vents	Post reactor Refrigerated condenser Water scrubber
Diamond Shamrock Deer Park, TX	Air	Oxychlorination vent Direct-chlorination vent Purification vents	Catalytic oxidizer Refrigerated condenser Vent condensers
La Porte, TX	Air	Process vents	Thermal oxidizer
Dow Freeport, TX	Not reported	Process vents	Thermal oxidizer
Oyster Creek, TX	Oxygen	Process vents	Thermal oxidizer
B.F. Goodrich Calvert City, KY	Air	Oxychlorination vent Direct-chlorination vent	Solvent absorption Refrigerated vent condenser

7-12

CONTINUED

TABLE 7-5. (continued)

Company and location	Process used	Emission sources	Control technique or device used
PPG Lake Charles, LA	Oxygen	Oxychlorination vent	Thermal oxidizer
		Direct-chlorination vent	
Guayanilla, PR	Oxygen	Process vents	Thermal oxidizer
Shell Deer Park, TX	Air	Oxychlorination vent Direct-chlorination vent Purification vents Storage vents	Post reactor } Thermal oxidizer
Vulcan Geismar, LA	Air	Oxychlorination vent Purification vents	Chilled water scrubber None

as feedstock. In the chlorination process, the feed materials and chlorine are combined at about 400°C (750°F), followed by hydrogen chloride by-product removal, product treatment and distillation, and recycle or incineration at the column ends. In oxychlorination, reaction of ethylene dichloride, chlorine or hydrogen chloride, and oxygen results in an initial product comprised of water, carbon dioxide, and hydrogen chloride, as well as perchloroethylene, trichloroethylene and by-product organics such as carbon tetrachloride. Water removal, hydrogen chloride absorption and inert gas purging result in a crude product which is refined further and neutralized.<sup>22</sup> Figures 7-4 and 7-5 show these process flows and related carbon tetrachloride emission points.

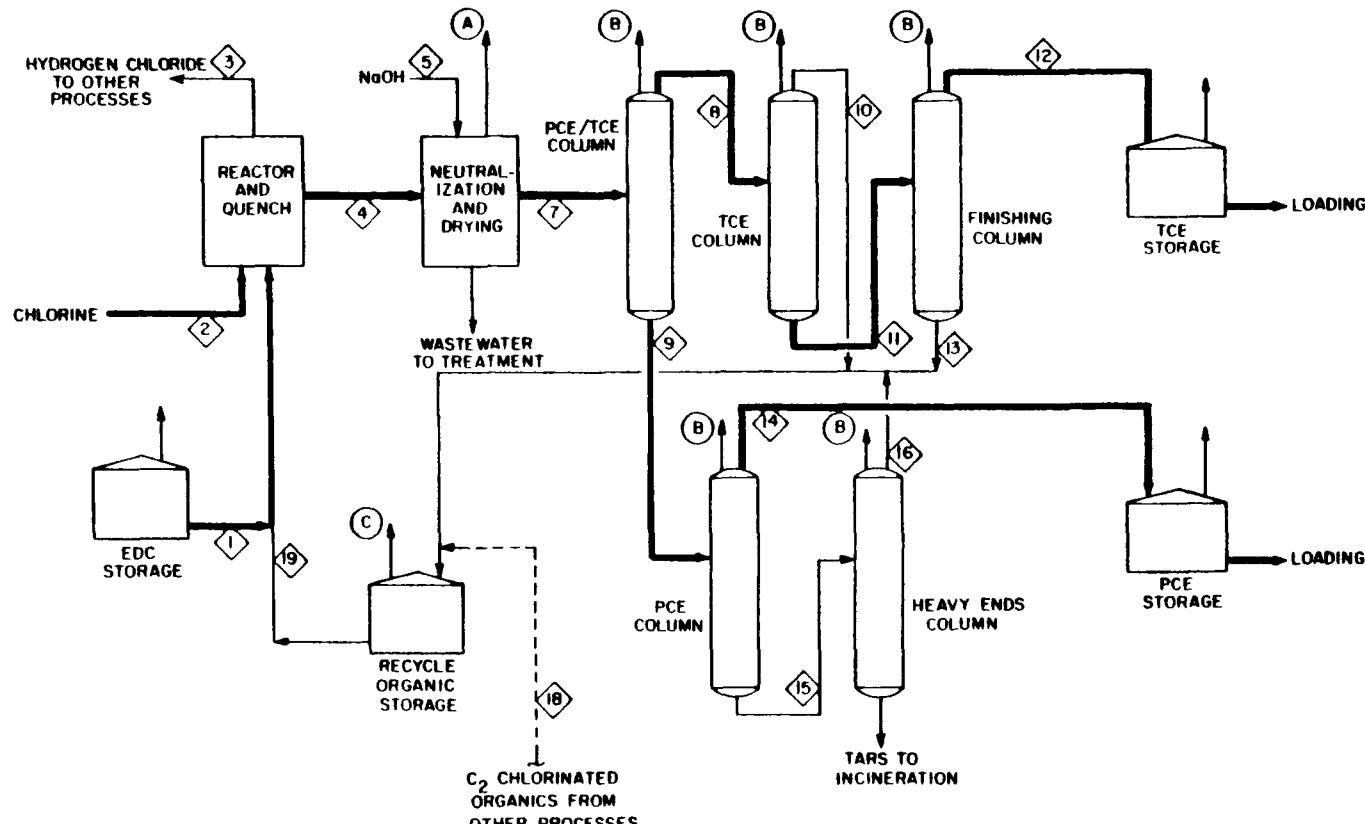
Process variations make it possible to direct production partly or entirely to either principal product. As shown in the list of producers, Table 7-6, two producers currently produce only one of the two possible principal products.

### 7.3.2 Carbon Tetrachloride Emissions

The only available emissions data for these processes are for the Diamond Shamrock plant, which produces only perchloroethylene.<sup>27</sup> Table 7-7 presents emission factors derived from those data. Carbon tetrachloride formation may be affected significantly by the process variations necessary to produce only perchloroethylene. It is not known how these emission factors might change for the other plants in Table 7-6.

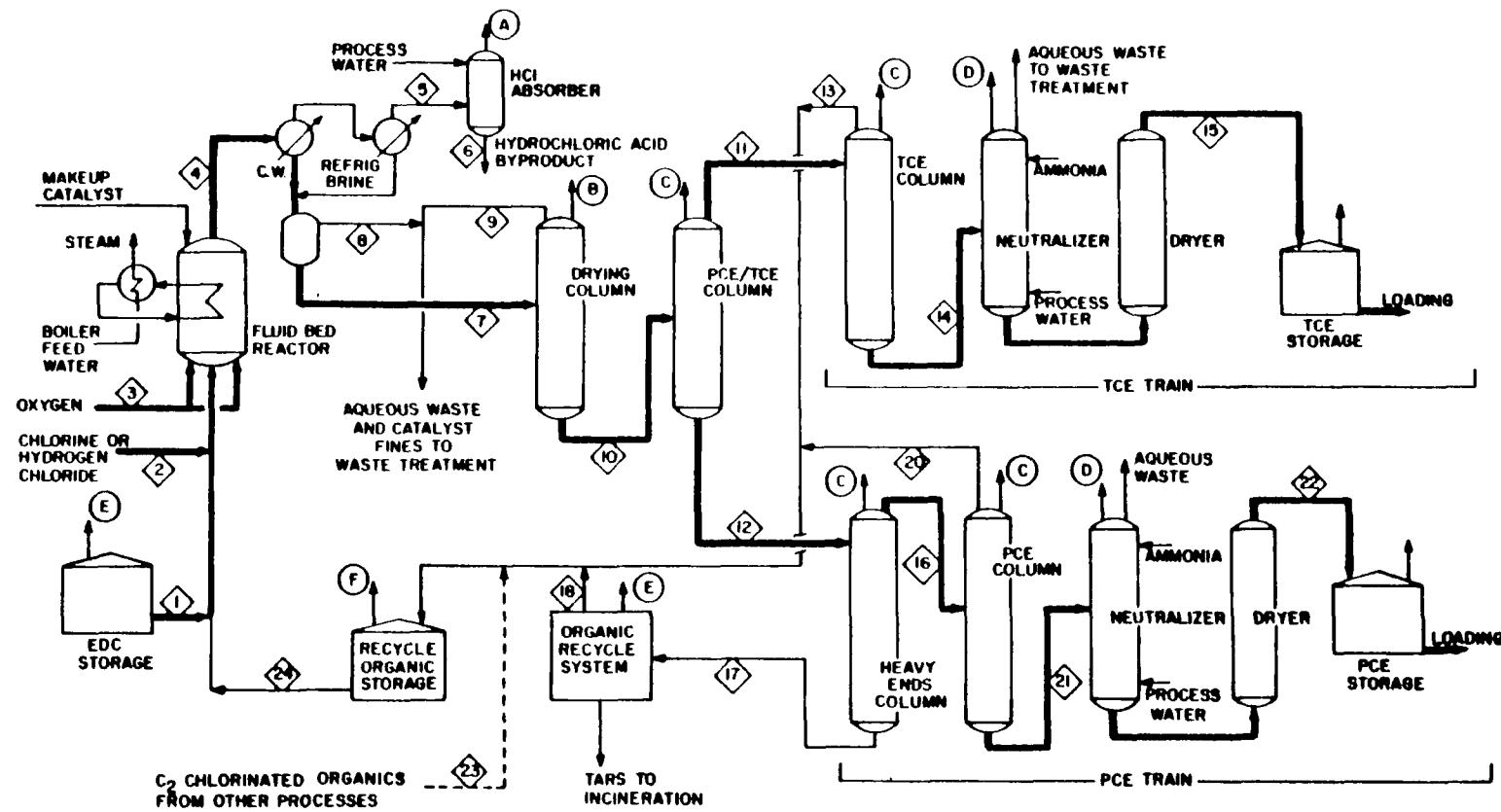
### 7.3.3 Emission Controls

The Diamond Shamrock plant has a chilled-water condenser on its drying column with an estimated 80 percent VOC reduction efficiency, and also uses various condensers on in-process and product storage. The Ethyl plant has a refrigerated condenser with 80 percent VOC control efficiency on its distillation column vents, after which vent gases are recycled into another process. The Dow plant is reported to use water scrubbers on process vents, but these will have a marginal effect on any carbon tetrachloride emissions. In-process storage is in pressurized tanks with regulators which are estimated to provide 70 percent control. PPG uses a thermal oxidizer on the HCl absorber and drying column vents



NOTE: Letters in this figure refer to process vents described in the text and tables. Numbers refer to process descriptions in the first reference cited below. Heavy lines indicate final product streams throughout the process.

Figure 7-4. Process flow diagram for perchloroethylene and trichloroethylene production by chlorination of ethylene dichloride.<sup>23,24</sup>



NOTE: Letters in this figure refer to process vents described in the text and tables. Numbers refer to process descriptions in the first reference cited below. Heavy lines indicate final product streams throughout the process.

Figure 7-5. Process flow diagram for perchloroethylene and trichloroethylene production by oxychlorination of ethylene dichloride.<sup>25,26</sup>

TABLE 7-6. PERCHLOROETHYLENE AND/OR TRICHLOROETHYLENE PRODUCTION BY CHLORINATION OF ETHYLENE DICHLORIDE<sup>a</sup>

EPA region	Company	Location	Annual capacity <sup>3</sup> (x10 <sup>3</sup> Mg) <sup>b</sup>		Ozone NAAQS attainment status <sup>4,5</sup>	Post-1982 attainment date granted? <sup>4,5</sup>
			Perchloro-ethylene	Trichloro-ethylene		
VI	Ethyl Corp.	Baton Rouge, LA	23	20	NA	No
	PPG Industries, Inc.	Lake Charles, LA	91	91	NA	No
	Diamond Shamrock Corp.	Deer Park, TX	75	c	NA	Yes
	Dow Chemical, U.S.A.	Freeport, TX	--	55	NA	No

<sup>a</sup>Does not include Vulcan plants at Geismar, LA and Wichita, KS which use ethylene dichloride with chlorination bottoms to produce perchloroethylene and carbon tetrachloride -- these plants are described under carbon tetrachloride producers.

<sup>b</sup>Includes only perchloroethylene and trichloroethylene produced from ethylene dichloride.

<sup>c</sup>Trichloroethylene capacity of 23 x 10<sup>3</sup> Mg/yr placed on standby in 1978.<sup>3</sup>

NA -- Nonattainment

TABLE 7-7. UNCONTROLLED CARBON TETRACHLORIDE EMISSION FACTORS  
FOR A PLANT PRODUCING PERCHLOROETHYLENE BY ETHYLENE  
DICHLORIDE CHLORINATION

Emission source	Uncontrolled carbon tetrachloride emission factor <sup>b</sup>
Process	
Neutralization	0.016 kg/Mg
Drying column	0.063 kg/Mg
Distillation column	0.027 kg/Mg
Light ends/heavy ends mix tank	0.039 kg/Mg
Storage - light ends	0.11 kg/Mg
Process fugitive <sup>b</sup>	2.8 kg/hr

<sup>a</sup>Emission factors in terms of kg/Mg refer to kg of carbon tetrachloride emitted per Mg of perchloroethylene produced, from Reference 28.

<sup>b</sup>Fugitive emission rate independent of plant rate.

as well as many other sources in other processes. Estimated VOC control of this unit is 99 percent. Water scrubbers used to control distillation and product neutralization vents will have little effect on VOC emissions.<sup>29</sup> Evaluation of the effect of these controls on carbon tetrachloride emissions is not possible with available data.

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## 8.0 GRAIN FUMIGANT FORMULATION AND USE

### 8.1 GENERAL INFORMATION

Air emissions of carbon tetrachloride occur during the formulation, storage, handling, application and subsequent release of liquid grain fumigant mixtures. Carbon tetrachloride is used in essentially all of the liquid grain fumigant mixtures available for application to stored grain.<sup>1</sup> While it is somewhat active against pests by itself, carbon tetrachloride is used as a carrier and to reduce risk of fire and explosion in the most common liquid grain fumigant formulations.<sup>2</sup> The most common formulations are:

- o Carbon tetrachloride 80 percent, carbon disulfide 20 percent;
- o Carbon tetrachloride 80.9 percent, carbon disulfide, 16 percent, ethylene dibromide 1.2 percent, sulfur dioxide 1.5 percent and pentane 0.4 percent;
- o Carbon tetrachloride 77.7 percent, carbon disulfide 15.4 percent, ethylene dibromide 5 percent, sulfur dioxide 1.5 percent and pentane 0.4 percent;
- o Carbon tetrachloride 60 percent, ethylene dichloride 35 percent, and ethylene dibromide 5 percent; and
- o Carbon tetrachloride 75 percent, ethylene dichloride 25 percent.<sup>2</sup>

The carbon tetrachloride/carbon disulfide formulation is estimated to account for 65 percent of all liquid fumigants, with the remaining 35 percent divided among the three mixtures containing ethylene dibromide. Use of the last formulation above is reported to be negligible.<sup>3</sup> One reference lists about 120 different brand names under which these products are distributed and sold, as well as about 65 facilities at which they

are formulated.<sup>4</sup> Since this listing provides no data which would allow estimation of carbon tetrachloride emissions, it is not included here. Combining all formulations, the following average distribution of major fumigant ingredients is reported for 1976-1979 in weight percent:<sup>5</sup>

Carbon tetrachloride	76.7 percent
Carbon disulfide	12.1 percent
Ethylene dichloride	7.1 percent
Ethylene dibromide	1.6 percent
Other ingredients	2.5 percent

The best available estimates for average annual carbon tetrachloride use in these products are 11,500 to 14,800 Mg (12,680 to 16,300 tons) between 1976 and 1979,<sup>6</sup> and 12,800 Mg (14,000 tons) for 1977 and 1978.<sup>7</sup> This estimate is based on actual application, and does not include any losses in formulation. Formulation and application are discussed individually below. It should be noted that this section covers only pesticides which actually include carbon tetrachloride. Carbon tetrachloride is also used in synthesis or processing of other pesticide and herbicide products, such as several of the miscellaneous sources discussed in Section 10.2.

## 8.2 LIQUID FUMIGANT FORMATION DESCRIPTION

Pesticide formulation systems typically are batch mixing operations, such as the one shown in Figure 8-1. Ingredients or solvents received in bulk are transferred to holding tanks for storage. Smaller-volume components are usually kept in the original container until needed.<sup>8</sup>

Batch mixing tanks are typically open-topped vessels fitted with an agitator. The mixing tank may also be equipped with a heating or cooling system. Ingredients are fed into the mix tank, with the quantity determined by meters, scales, or by measuring the level in the mix tank. Other blending agents (such as emulsifiers) may be added directly to the mix tank. The formulated material may be filtered by cartridge or polishing filters and pumped to a holding tank before being put into containers

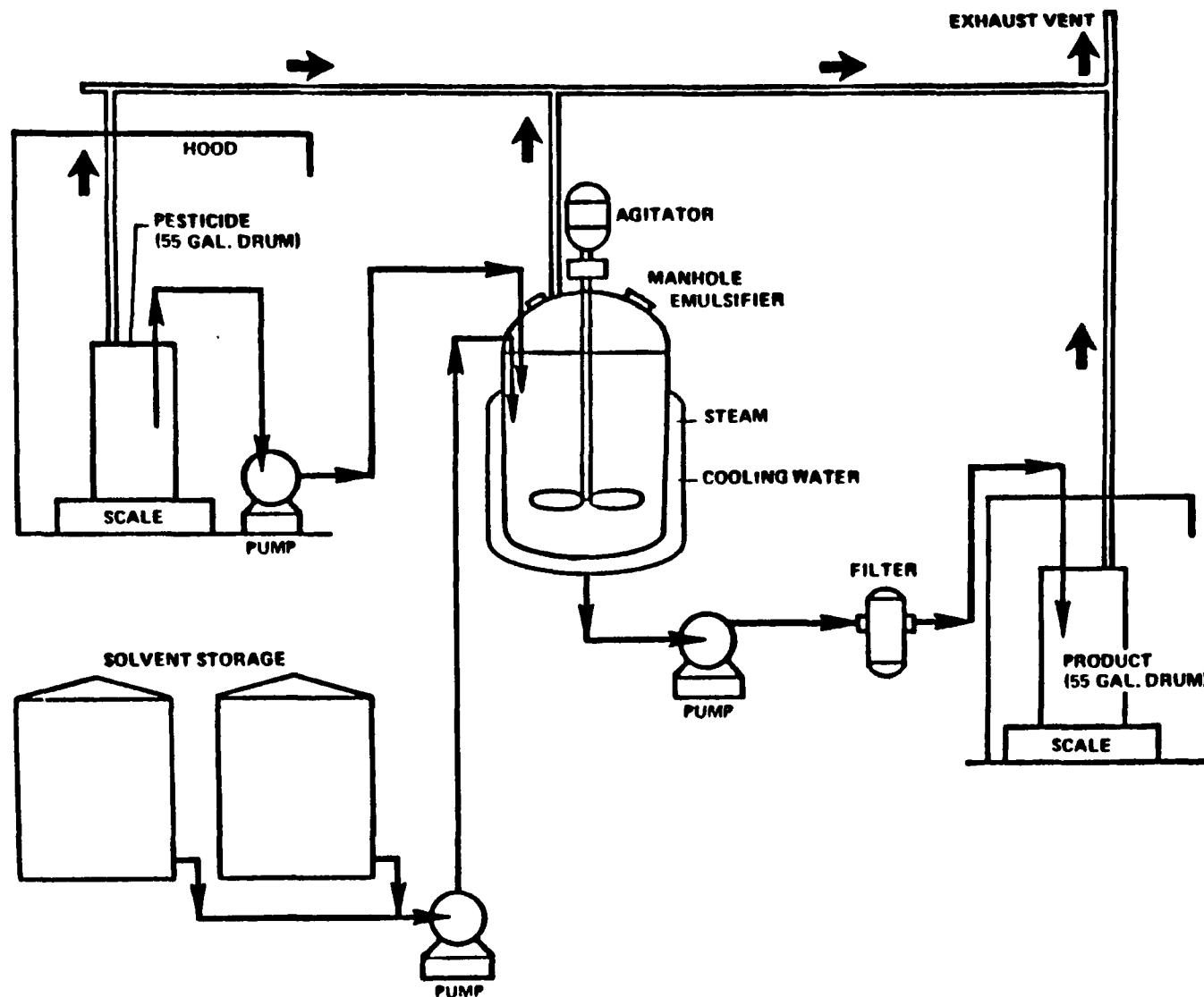


Figure 8-1. Process flow diagram for liquid pesticide formulation.<sup>8</sup>

for shipment. Storage and holding tanks, mixing tanks and container-filling lines are provided with an exhaust connection or hood to remove any vapors. The exhaust from the system is vented to a scrubber or directly to the atmosphere.<sup>8</sup>

Sources of carbon tetrachloride emissions from pesticide formulation include storage vessels, mixing vessel vents, and leaks from pumps, valves, and flanges.<sup>8</sup> There is not sufficient information for the development of carbon tetrachloride emission factors for liquid fumigant formulation facilities.

### 8.3 LIQUID FUMIGANT APPLICATION DESCRIPTION

Liquid fumigants based on carbon tetrachloride are used to control insect infestations during storage, transfer, milling, distribution and processing of grain. They are applied to grain in on-farm storage, at subterminal, terminal and port elevators, at mill holding facilities, and in transport vehicles. In addition to storage, about two percent of all carbon tetrachloride formulations are used to fumigate grain mill equipment.<sup>9</sup>

Almost all on-farm grain fumigation is done with carbon tetrachloride-based liquid formulations. The principal alternative fumigant, aluminum phosphide, is applied in pellets or tablets which release phosphine gas, the actual active ingredient. Phosphine escapes quickly from typical loosely-constructed on-farm storage facilities, and must be applied by trained, certified personnel. Thus, it has been used very little on farms. Use of aluminum phosphide is more common at off-farm storage facilities, due to tighter construction, availability of trained personnel, and the ability to turn stored grain, facilitating uniform distribution of the fumigant tablets. It has been estimated that aluminium phosphide is used on 70 percent of the grain fumigated in large elevators.<sup>10</sup>

Thus the proportion of use of carbon tetrachloride formulations is greatest on the farm and at loosely-constructed smaller elevators, while terminal and port elevators are more likely to use aluminum phosphide formulations. The low reactivity of aluminium phosphide formulations at low ambient temperatures leads to the increased use of carbon tetrachloride

formulations at off-farm storage facilities in the winter. Carbon tetrachloride formulations are also the most practical fumigants for grain in transit, since they can be applied to the surface of the load and are effective at all temperatures. The best available estimates of the distribution of fumigant use are for 1977. They indicate that about 3,900 Mg (4,300 tons) of carbon tetrachloride were used in on-farm grain storage, while about 8,900 Mg (9,800 tons) were used at off-farm facilities.<sup>11</sup> Average application rates for various grains were used with these usage figures to estimate that liquid fumigants were applied to 6.4 to 11.7 percent of total U.S. grain production from 1976 to 1979.<sup>12</sup> These average application rates are shown in Table 8-1.

TABLE 8-1. FUMIGANT APPLICATION RATES<sup>13</sup>

Grain	Application rate (gal/10 <sup>3</sup> bu)	
	On-farm	Off-farm
Wheat	3 - 4	2 - 3
Corn	4 - 5	3 - 4
Rice, Oats, Barley, Rye	3 - 4	2 - 3
Grain sorghum	5 - 6	4 - 5

Liquid fumigants typically are applied by the "gravity distribution" method, which consists of pouring or spraying the liquid on the surface of stored grain. This may be done to the entire stored mass, or to individual layers, and may occur as grain is first stored, or upon turning (shifting from one storage facility to another). Grain in railroad cars may be treated by pouring the fumigant through roof vents or by spraying it into the car with a power sprayer. In addition to hand application and pumped or pressurized delivery systems, metering devices are also used to treat streams of moving grain.<sup>14</sup>

After application of liquid fumigants, grain must be left undisturbed for a few days to allow diffusion and proper pesticidal action. In most cases, the grain is not disturbed until turning or transfer is necessary. At some facilities, release of the fumigant after an adequate treatment period may be facilitated by turning the grain or by ventilating tightly-sealed facilities with fresh air.<sup>15</sup>

Emissions of carbon tetrachloride from fumigant mixtures occur during fumigant application, and when fumigated grain is exposed to the atmosphere, during storage, turning, ventilation, or loading. Because of the relatively high vapor pressure of carbon tetrachloride, it is estimated that essentially all carbon tetrachloride used in fumigants evaporates. The time rate of emissions is highly variable and depends on the application rate, the type of storage (whether loose or tight-fitting), the manner in which the grain is handled and the rate of release of fumigant residues on and in the grain. Figure 8-2 presents the results of a laboratory study of the level of residual carbon tetrachloride fumigant on wheat as a function of the number of days since aeration.<sup>16</sup> The grain was fumigated and aerated under conditions comparable to commercial fumigation and aeration conditions.<sup>17</sup>

Specific information on geographic distribution of fumigant use does not appear to be available. Tables 8-2 and 8-3 provide statistics on on-farm and off-farm grain storage facilities and capacities by State. Fumigant use is not distributed evenly by production or storage capacity, because the degree to which stored grain is subject to attack by pests is highly dependent on temperature and humidity. For example, in on-farm storage, insects can be a serious problem throughout the storage period in the southern States, while little if any damage would be expected in the first season's storage in drier northern States.<sup>20</sup>

#### 8.4 REGULATIONS AND EMISSION CONTROL

The EPA Office of Pesticide Programs issued a Notice of Rebuttable Presumption Against Registration (RPAR) on October 15, 1980<sup>4</sup> for all pesticide products containing carbon tetrachloride. While further action under this RPAR may lead to a significant reduction or elimination

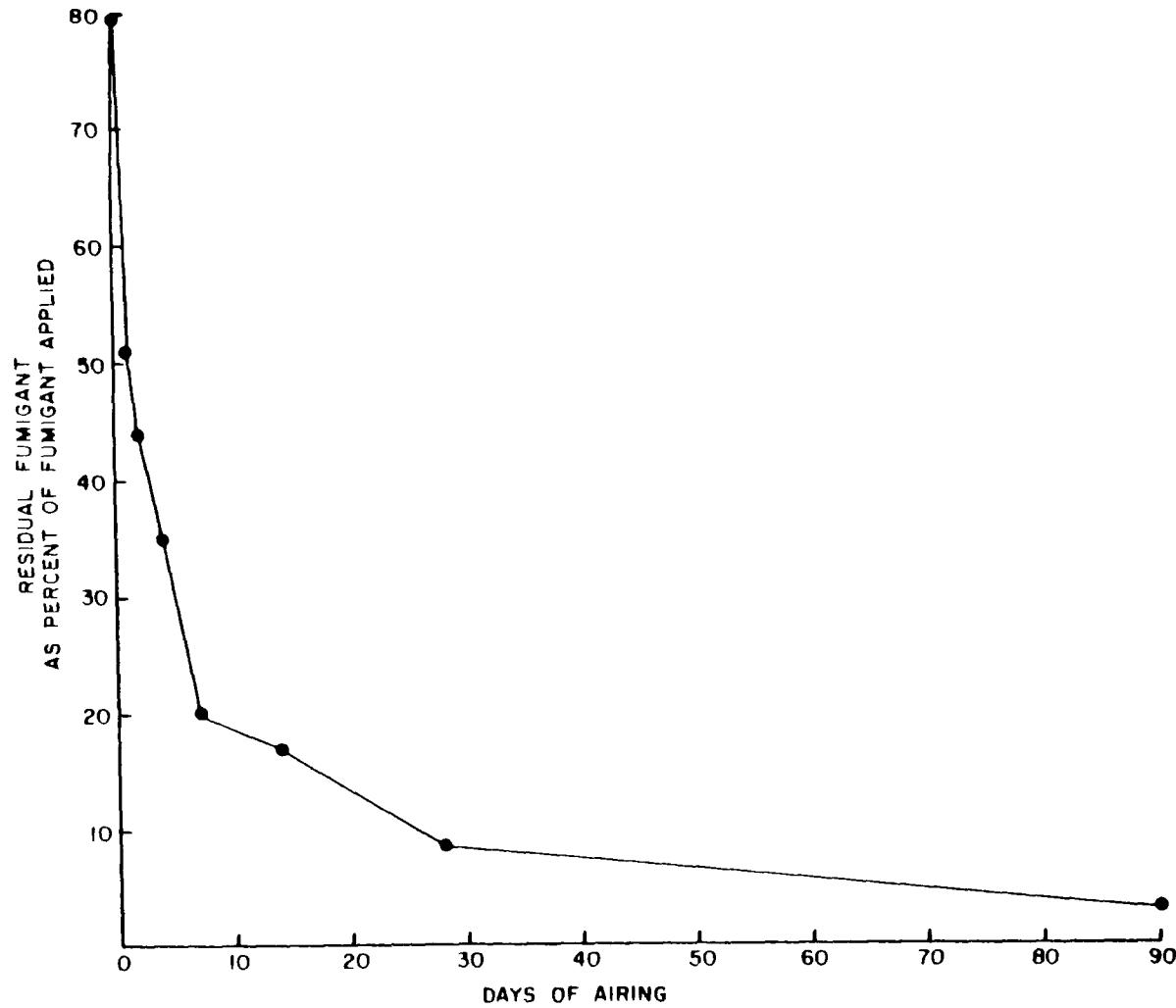


Figure 8-2. Residual carbon tetrachloride fumigant as a function of days grain aired.<sup>16</sup>

TABLE 8-2. ON-FARM GRAIN STORAGE<sup>18</sup>

Region and State	Capacity (10 <sup>3</sup> bu)	Regional percentage
<u>Northeast:</u>	<u>142,698</u>	<u>2%</u>
Maine	2,866	
New Hampshire	0	
Vermont	0	
Massachusetts	9,654	
Rhode Island	0	
Connecticut	222	
New York	39,204	
New Jersey	5,190	
Pennsylvania	62,498	
Delaware	2,057	
Maryland	21,007	
<u>Lake States:</u>	<u>1,357,627</u>	<u>17%</u>
Michigan	116,462	
Wisconsin	244,827	
Minnesota	996,338	
<u>Corn Belt:</u>	<u>2,982,755</u>	<u>37%</u>
Ohio	225,279	
Indiana	429,981	
Illinois	947,208	
Iowa	1,071,203	
Missouri	309,084	
<u>Northern Plains:</u>	<u>2,132,264</u>	<u>26%</u>
North Dakota	681,397	
South Dakota	394,381	
Nebraska	715,594	
Kansas	340,892	
<u>Appalachian:</u>	<u>236,607</u>	<u>3%</u>
Virginia	37,554	
West Virginia	5,685	
North Carolina	100,938	
Kentucky	49,237	
Tennessee	43,193	
<u>Southeast:</u>	<u>159,132</u>	<u>2%</u>
South Carolina	31,437	
Georgia	87,720	
Florida	12,145	
Alabama	27,830	

CONTINUED

TABLE 8-2. (continued)

Region and State	Capacity (10 <sup>3</sup> bu)	Regional percentage
<u>Delta States:</u>	<u>131,593</u>	<u>1%</u>
Mississippi	41,588	
Arkansas	50,095	
Louisiana	39,910	
<u>Southern Plains:</u>	<u>315,157</u>	<u>4%</u>
Oklahoma	76,685	
Texas	238,472	
<u>Mountain:</u>	<u>507,357</u>	<u>6%</u>
Montana	278,783	
Idaho	77,960	
Wyoming	19,519	
Colorado	97,216	
New Mexico	9,136	
Arizona	6,404	
Utah	15,220	
Nevada	3,119	
<u>Pacific:</u>	<u>151,622</u>	<u>2%</u>
Washington	60,011	
Oregon	33,552	
California	58,059	
Total	8,116,812	100%

TABLE 8-3. OFF-FARM GRAIN STORAGE<sup>19</sup>

State	Number of facilities	Capacity (10 <sup>3</sup> bu)
Alabama	37,290	178
Arizona	33,890	76
Arkansas	179,180	283
California	115,710	226
Colorado	91,500	209
Delaware	17,200	27
Florida	6,070	27
Georgia	56,700	344
Idaho	64,070	231
Illinois	775,260	1,177
Indiana	245,550	804
Iowa	635,000	1,141
Kansas	830,000	1,086
Kentucky	49,580	202
Louisiana	87,010	131
Maryland	36,940	64
Michigan	90,240	351
Minnesota	366,440	894
Mississippi	76,350	183
Missouri	204,140	611
Montana	54,000	298
Nebraska	484,600	740
Nevada	300	4
New Jersey	2,200	24
New Mexico	17,550	27
New York	70,270	243
North Carolina	63,420	465
North Dakota	140,070	580
Ohio	228,800	713
Oklahoma	203,520	400
Oregon	65,530	238
Pennsylvania	26,900	337
South Carolina	33,470	177
South Dakota	83,820	386
Tennessee	43,180	106
Texas	720,350	896
Utah	17,170	55
Virginia	29,920	241
Washington	186,370	324
West Virginia	530	9
Wisconsin	118,920	428
Wyoming	5,580	49
Other States	5,170	80
Total	6,600,030	15,065

of the use of carbon tetrachloride in fumigants, the possible outcome of the RPAR process is not known. Existing measures for reduction of air emissions of these fumigants might include expanded use of alternatives such as aluminum phosphide and more efficient use of the currently-used formulations. Implementation of either of these control measures could involve a combination of storage facility modifications (such as improving existing grain storage structures and installing ventilation/recirculation systems), and improved work practices, which might be possible through application guidelines and applicator training/certification.

## 8.5 REFERENCES

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## 9.0 PHARMACEUTICAL MANUFACTURING

### 9.1 SOURCE DESCRIPTION

Carbon tetrachloride is used as a solvent in the manufacturing of pharmaceutical products. There are approximately 800 pharmaceutical plants producing drugs in the United States and its territories. Most of the plants are small and have less than 25 employees. Nearly 50 percent of the plants are located in five States: 12 percent in New York; 12 percent in California; 10 percent in New Jersey, 5 percent in Illinois; and 6 percent in Pennsylvania. These States also contain the largest plants in the industry. Puerto Rico has had the greatest growth in the past 15 years, during which 40 plants have located there. Puerto Rico now contains 90 plants or about 7.5 percent of the total. EPA's Region II (New Jersey, New York, Puerto Rico, Virgin Islands) has 340 plants (28 percent of the total); Region V (Illinois, Minnesota, Michigan, Ohio, Indiana, Wisconsin) 215 plants (20 percent); and Region IX (Arizona, California, Hawaii, Guam, American Samoa) 143 plants (13 percent).<sup>1</sup> Data on geographic distribution of carbon tetrachloride use at these plants are not available.

Synthetic pharmaceuticals are normally manufactured in a series of batch operations. Figure 9-1 presents a typical flow diagram for a batch synthesis operation. To begin a production cycle, the reactor is water washed and dried with a solvent. Air or nitrogen is usually used to purge the tank after it is cleaned. Solid reactants and solvent are then charged to the reactor. After the reaction is complete, any remaining unreacted volatile compounds and solvents are removed from the reactor by distillation and condensed. The pharmaceutical product is then transferred to a holding tank. In the holding tank, the product may be washed three to four times with water or solvent to remove any remaining reactants and by-products. The solvent used in washing generally is

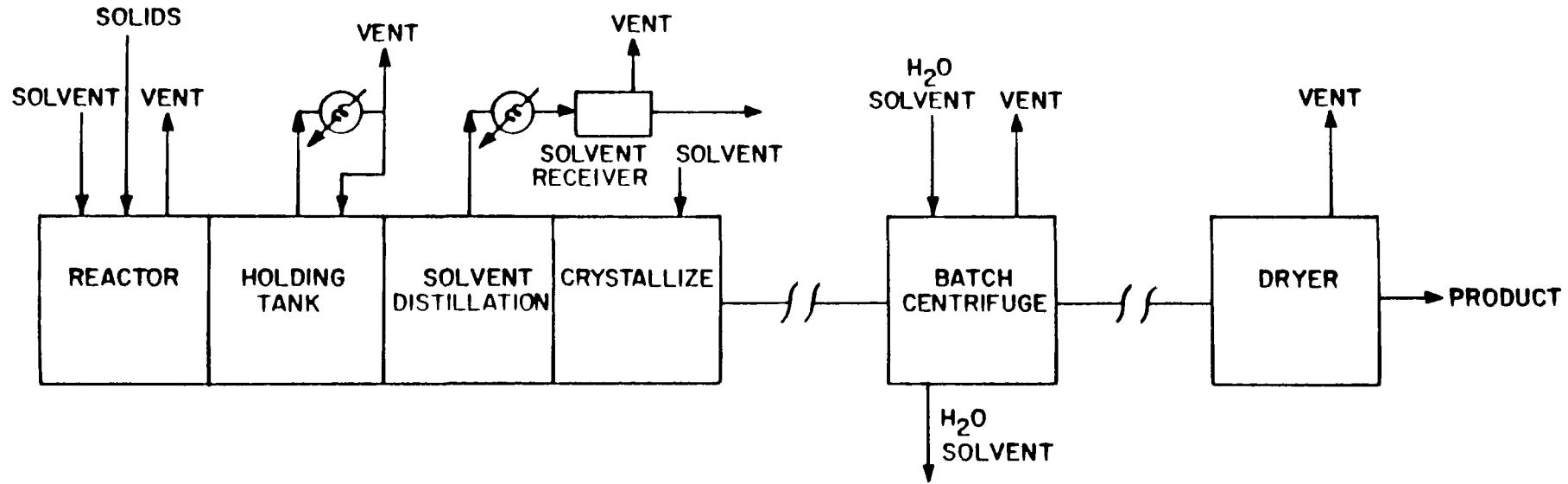


Figure 9-1. Process diagram for typical synthetic pharmaceutical manufacturing process.<sup>2</sup>

evaporated from the reaction product. The crude product may then be dissolved in another solvent and transferred to a crystallizer for purification. After crystallization, the solid material is separated from the remaining solvent by centrifuging. While in the centrifuge, the product cake may be washed several times with water or solvent.

Tray, rotary, or fluid-bed dryers are employed for final product finishing.<sup>3</sup>

## 9.2 PHARMACEUTICAL MANUFACTURING SOLVENT EMISSION SOURCES

Where carbon tetrachloride is used as a solvent in the manufacture of a pharmaceutical product, each step of the manufacturing process may be a source of carbon tetrachloride emissions. The magnitude of emissions can be expected to vary widely within and among operations, but information on individual operations involving carbon tetrachloride does not exist. Therefore, it is impossible to cite typical emission rates for various operations. An approximate ranking of emission sources has been established and is presented below in order of decreasing emission significance. The first four sources typically account for the majority of emissions from a plant.

1. Dryers
2. Reactors
3. Distillation units
4. Storage and transfer
5. Filters
6. Extractors
7. Centrifuges
8. Crystallizers

A survey of 26 ethical drug manufacturers published in 1978<sup>5</sup> cites a total annual carbon tetrachloride purchase of 1,850 Mg (2,030 tons) by these manufacturers. The survey was estimated to cover about 85 percent of all volatile organic compounds used by the reporting manufacturers, who accounted for 53 percent of domestic sales of ethical pharmaceuticals in 1975. Estimated final disposition of the above total carbon tetrachloride

usage was reported as 210 Mg (230 tons) air emissions (11 percent), 120 Mg (130 tons) sewer disposal (7 percent) and 1,510 Mg (1,660 tons) incineration (82 percent). The survey did not provide data on individual plants, processes, or related carbon tetrachloride use.

### 9.3 EMISSION CONTROLS

Condensers, scrubbers, and carbon adsorbers can be used to control emissions from all the emission sources listed in Section 9.2. Storage and transfer emissions can also be controlled by the use of vapor return lines, conservation vents, vent scrubbers, pressurized storage tanks, and floating roof storage tanks. This source category is the subject of a Group II Control Techniques Guideline, which cites the above control techniques.<sup>6</sup> Although control efficiencies may vary with the specific process, overall control of 90 percent of carbon tetrachloride emissions or better should be achievable for most processes.

#### 9.4 REFERENCES

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3. Reference 1, p. 2-2.
4. Reference 1, p. 2-5.
5. Reference 1, Appendix A.
6. Reference 1, Chapters 3 and 4.

## 10.0 OTHER POTENTIAL SOURCES OF CARBON TETRACHLORIDE EMISSIONS

This section summarizes information on other reported or potential sources of carbon tetrachloride air emissions identified during the data-gathering phase of this study. Many of these sources may be relatively small and some appear to be one-of-a-kind plants. However, there are several which may have fairly high individual or collective emissions relative to other identified carbon tetrachloride sources. Only limited verification and follow-up of these preliminary source identifications was possible.

### 10.1 PHOSGENE/ISOCYANATE/POLYURETHANE PROCESSES

Phosgene is produced by reacting chlorine gas and carbon monoxide in the presence of activated carbon, at  $200^{\circ}\text{C}$  ( $390^{\circ}\text{F}$ ). Hot reactor effluent gases are condensed to remove most of the phosgene, and then are scrubbed with a hydrocarbon solvent to remove entrained phosgene.<sup>1</sup> As indicated by the list of phosgene producers in Table 10-1, almost all of the phosgene produced in this country is used directly in other operations at the same plant. The principal use is in manufacture of isocyanates, which are then used in making polyurethane resins.

A 1977 emission inventory by the West Virginia Air Pollution Control Commission cited by A.D. Little<sup>3</sup> indicates that carbon tetrachloride is used as the absorbent in a scrubber which is part of the phosgene production process at the Union Carbide plant at Institute, West Virginia. Identified as Process 25S, the carbon tetrachloride sources cited included two storage tanks of unknown size with total estimated emissions of 98.6 Mg/yr (108.5 tons/yr) and a unit appearing to be a scrubber which had estimated emissions of 10.7 Mg/yr (11.8 tons/yr) and a temperature of  $300^{\circ}\text{C}$  ( $570^{\circ}$ ). Except for inconsistencies in the temperatures involved, these data are consistent with typical scrubbing of non-condensable gases with hydrocarbon solvent after the primary post-reactor condenser in phosgene production.

TABLE 10-1. PHOSGENE PRODUCERS<sup>2</sup>

EPA region	Company	Location	Phosgene production capacity ( $\times 10^3$ Mg)
II	DuPont	Deepwater, NJ	81
	Van De Mark	Lockport, NY	4 <sup>a</sup>
III	Essex	Baltimore, MD	4
	Mobay	New Martinsville, WV	111
V	Olin	Moundsville, WV	45
	Union Carbide	Institute, WV	64
	General Electric	Mount Vernon, IN	41
VI	PPG	Barberton, OH	2
	BASF Wyandotte	Geismar, LA	25
	ICI Americas	Geismar, LA	68
	Olin	Lake Charles, LA	55
	Dow	Freeport, TX	59
	Mobay	Cedar Bayou, TX	114
	PPG	La Porte, TX	30 <sup>a</sup>
	Upjohn	La Porte, TX	136
TOTAL			839

<sup>a</sup>These two plants are believed to be the only ones producing phosgene for sale; All others produce for captive consumption.

A Texas emission inventory<sup>4</sup> cites a carbon tetrachloride emission source of about 0.46 Mg/yr (0.51 tons/yr) as part of a toluene diisocyanate production process at the Dow Plant "B" at Freeport, Texas. This may be another example of carbon tetrachloride scrubbing of a phosgene process stream, which would be considered part of the isocyanate production. This plant was also reported to have a carbon tetrachloride storage tank emitting 0.9 Mg/yr (1.0 tons/yr), and a 9.3 Mg/yr (10.2 tons/yr) carbon tetrachloride source in a latex production. This latex may be a further step in the same sequence, such as an intermediate stage in polyurethane processing.

## 10.2 PESTICIDE PRODUCTION

Emissions of carbon tetrachloride were reported to be associated with several pesticide production operations, beyond the use of carbon tetrachloride as a major ingredient of grain fumigants discussed earlier. Carbon tetrachloride is apparently used as a solvent or reaction medium in these processes, which are discussed individually below.

Chlorothalonil: Chlorothalonil is also known by the Diamond Shamrock tradenames Daconil, Forturf, Termil and Bravo, and as tetrachloro-isophthalonitrile; 2,4,5,6-tetrachloro-1,3-benzenedicarbonitrile; and 1,3-dicyano-2,4,5,6-tetrachlorobenzene.<sup>5,6</sup> Cited uses include agricultural and horticultural fungicide, bactericide and nematocide.<sup>5</sup> It is made by dissolving tetrachloroisophthalic acid chloride in an organic solvent and adding ammonia. A wide range of solvents can be used, although one reference cites xylene or dioxane as preferred solvents.<sup>6</sup>

Carbon tetrachloride is probably used as the solvent or in subsequent product refinement steps at the Diamond Shamrock Daconil plant at Houston, Texas. The 1980 Texas emission inventory cites two emission points at this plant as emitting 133 and 87 Mg/yr (143 and 96 tons/yr) of carbon tetrachloride, respectively.<sup>4</sup> This plant, also cited as being in Greens Bayou, is reported to be the only one in the U.S. producing chlorothalonil.<sup>2</sup>

Linuron: Linuron is a DuPont tradename for N'-(3,4-dichlorophenyl)-N-methoxy-N-methylurea, also known as DuPont Herbicide 326 and Lorox. Its principal use is as a selective herbicide.<sup>7,8</sup> Production locations are reported to include DuPont plants at East Chicago, Illinois, and LaPorte, Texas.<sup>2</sup> The 1980 Texas emission inventory cites the LaPorte plant as emitting 1.9 and 0.7 Mg/yr (2.1 and 0.8 tons/yr) of carbon tetrachloride from two emission points associated with the Linuron process.<sup>4</sup> One process description indicates use of benzene as a solvent for the two feed materials, O,N-dimethyl-hydroxylamine and 3,4-dichlorophenylisocyanate. Air emissions of 0.5 kg hydrocarbon solvent per megagram (1 lb/ton) of Linuron product were also cited by this source.<sup>8</sup> It may be that carbon tetrachloride has been substituted for benzene as the hydrocarbon solvent in this process.

Sulfuryl flouride: Sulfuryl flouride is an insecticidal fumigant marketed by Dow Chemical under the tradename Vikane. It can be produced by heating barium fluorosulfonate to produce barium sulfate and sulfuryl flouride, or by burning flourine in sulfur dioxide.<sup>9</sup> It is produced at the Dow plant in Pittsburg, California.<sup>2</sup> A contact at the Bay Area Air Quality Management District indicates that this process is a source of carbon tetrachloride air emissions,<sup>10</sup> but no additional information was available.

#### 10.3 HYPALON<sup>®</sup> SYNTHETIC RUBBER PROCESS

Hypalon is the tradename for a DuPont synthetic rubber which is produced by reacting polyethylene with chlorine and sulfur dioxide, transforming the thermoplastic polyethylene into a vulcanizable elastomer. The reaction is conducted in a solvent reaction medium.<sup>11</sup> A Texas emission inventory for 1980 includes eight emission points for carbon tetrachloride at the DuPont plant at Beaumont, Texas. The cited emissions range from 1 to 65 Mg/yr (1.1 to 72 tons/yr), totalling 105 Mg/yr (116 tons/yr).<sup>4</sup> This plant is apparently the only one in the U.S. producing Hypalon.<sup>2</sup>

#### 10.4 CARBON TETRABROMIDE PRODUCTION

Carbon tetrabromide is produced by reaction of carbon tetrachloride and aluminum tribromide at about  $100^{\circ}\text{C}$  ( $212^{\circ}\text{F}$ ).<sup>12</sup> Carbon tetrachloride emissions are likely to occur from process waste streams as well as from raw material storage. The three plants listed in Table 10-2 are reported to produce carbon tetrabromide.<sup>2</sup> A Texas emission inventory for 1980 does not mention carbon tetrabromide production or carbon tetrachloride storage at the Diamond Shamrock plant at Deer Park.<sup>4</sup> There are three emission points, each described only as an "organic recovery systems," with carbon tetrachloride emissions of 0.87, 0.86, and 0.008 Mg/yr (0.96, 0.95, and 0.009 tons/yr), respectively. It is not known whether one or more of these recovery systems is associated with the carbon tetrabromide production. No information could be located on the Great Lakes Chemical Corp. plant at El Dorado, Arkansas, through the Arkansas Department of Pollution Control and Ecology.<sup>15</sup> New York Division of Air records on the Olin plant at Rochester do not mention carbon tetrabromide production, although a carbon tetrachloride storage tank with annual uncontrolled emissions of about 91 kg (200 pounds) and 99 percent control by carbon adsorption is registered. A number of other sources emitting very small amounts of carbon tetrachloride, in the range of 0.07 kg/yr (0.15 lb/yr), were reported for this plant.<sup>16,17</sup>

TABLE 10-2. CARBON TETRABROMIDE PRODUCERS

EPA region	Company	Location	Ozone NAAQS Attainment status <sup>13,14</sup>	Post-1982 attainment date granted? <sup>13,14</sup>
II	Olin Corporation	Rochester, NY	NA	No
VI	Great Lakes Chemical Corporation	El Dorado, AR	A	--
VI	Diamond Shamrock Corporation	Deer Park, TX	NA	Yes

A--Attainment

NA--Nonattainment

## 10.5 MISCELLANEOUS

The 1980 Texas emission inventory also reported the following carbon tetrachloride sources.<sup>4</sup>

Chlorine liquefaction: A chlorine liquefaction operation at the Diamond Shamrock facility in Deer Park, Texas, was reported to emit about 61 Mg/yr (67 tons/yr) of carbon tetrachloride from one point source. One description of the chlorine liquefaction process does not indicate any specific potential sources of carbon tetrachloride emission.<sup>18</sup> Carbon tetrachloride may be part of a noncondensable by-product stream cited in this reference as amounting to 20 kg per Mg (40 lbs per ton) of product chlorine.

Resinous chlorowax production: Three emission points associated with a resinous chlorowax process at Diamond Shamrock facility in Deer Park, Texas were reported to have total carbon tetrachloride emissions of about 9 Mg/yr (10 tons/yr).

Tetrachloropyridine/picolinic acid processes: Four emission points at the Dow Chemical Plant "A" in Freeport, Texas, were cited as having total carbon tetrachloride emissions of about 0.6 Mg/yr (0.7 tons/yr). Two of these points were in a symmetrical tetrachloropyridine process, and two were in a 4-amino-3,5,6-trichloropicalinic acid process. These chemicals are closely related, and may be part of the production process for a Dow product called N-Serve (2-chloro-6-(trichloromethyl)pyridine). N-Serve is a fertilizer additive used to control nitrification and prevent loss of soil nitrogen.<sup>19</sup>

Miscellaneous storage and loading: The Texas emission inventory included several entries for carbon tetrachloride storage and loading at tank farms not affiliated with carbon tetrachloride producers. One tank at GATX Terminals Corp. and one loading operation at PAK Tank Gulf Coast Inc. were each cited as having 1 Mg/yr (1.1 tons/yr) carbon tetrachloride emissions, while several other entries for these companies had no emissions reported.

A retrieval from the New Jersey Air Pollution Enforcement Data System indicated several reported carbon tetrachloride emission points related to several polymer productions and one dye production process.<sup>20,21</sup> Other potential carbon tetrachloride sources which could not be verified include laboratory uses, metal cleaning, production of paint, adhesives, textiles, and embalming supplies.

## 10.6 REFERENCES

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APPENDIX A  
BASES FOR CARBON TETRACHLORIDE EMISSION ESTIMATES

This Appendix provides examples of calculations and other details for emission estimates in Chapters 3 through 6. Many examples apply to similar estimates in more than one chapter, and the specific sections or tables are indicated. For information taken from the text, no references are supplied here.

1. Capacity Apportionment in Two-Process Carbon Tetrachloride Plants  
(Table 3-3)

Example: Plant 6 (Dow/Freeport)

Perchloroethylene co-product model plant produces 62.5 percent perchloroethylene, 37.5 percent carbon tetrachloride. Plant 6 perchloroethylene capacity is 68,000 Mg/yr. Assumed perchloroethylene co-product process carbon tetrachloride capacity calculated as:

$$\frac{(68,000 \text{ Mg/yr})}{0.625} \times 0.375 = 40,800 \text{ Mg/yr}$$

Total carbon tetrachloride capacity is 61,000 Mg; carbon tetrachloride production by methane chlorination calculated by subtraction:

$$61,000 \text{ Mg/yr} - 40,800 \text{ Mg/yr} = 20,200 \text{ Mg/yr}$$

2. Plant Capacity Factor (Tables 3-4, 4-2, 6-4)

Example: Plant 6 (Dow/Freeport)

Carbon tetrachloride production by perchloroethylene co-product process estimated at 40,800 Mg/yr; model plant produces 30,000 Mg/yr. Plant capacity factor calculated as follows:

$$\frac{40,800 \text{ Mg/yr}}{30,000 \text{ Mg/yr}} = 1.36$$

3. Uncontrolled Model Plant Emissions (Tables 3-5, 4-4, 6-5)

Example: Perchloroethylene Co-product Model Plant Process Emissions  
(Table 3-5)

Emission factor for process emissions is 0.0058 kg/Mg (Table 3-2), model plant capacity is 30,000 Mg/yr of carbon tetrachloride. Model plant emissions are:

$$\frac{0.0058 \text{ kg/Mg} \times 30,000 \text{ Mg/yr}}{1000 \text{ kg/Mg}} = 0.17 \text{ Mg/yr}$$

4. Uncontrolled Emissions (Tables 3-5, 4-4, 6-6)

Example: Plant 6 (Dow/Freeport) Perchloroethylene Co-Product Process Emissions (Table 3-5)

Model perchloroethylene co-product process emissions are 0.17 Mg/yr, plant capacity factor for Plant 6 is 1.36, industry-wide capacity utilization is 0.68, and estimated process emissions are:

$$0.17 \text{ Mg/yr} \times 1.36 \times 0.68 = 0.16 \text{ Mg/yr}$$

5. Controlled Emissions (Tables 3-12, 13; 4-7, 8; 5-3, 5; 6-11, 12)

Example: Plant 6 (Dow/Freeport) Option 2 Perchloroethylene Co-product Process Emissions (Table 3-13)

Calculation is identical to (4), above, with 90 percent control added (0.10 controlled emission factor):

$$0.17 \text{ Mg/yr} \times 1.36 \times 0.68 \times 0.10 = 0.02 \text{ Mg/yr}$$

6. Calculation of Emissions from Storage of Carbon Tetrachloride in a Fixed Roof Tank (Table 6-7)

In this appendix, working and breathing losses are calculated for a typical fixed roof storage tank containing carbon tetrachloride. Working and breathing losses are added to obtain an estimate for total losses from the tank. Since 90 percent control of working losses has been predicted as a result of the use of vapor balance, the percentage of total emissions accounted for by working losses is then multiplied by 90 percent to obtain an overall storage control efficiency for vapor balance, for Table 6-7.

The equations used to calculate breathing and working losses are as follows:<sup>1</sup>

1.  $L_T = L_B + L_W$
2.  $L_B = 1.02 \times 10^{-5} M \left( \frac{P}{14.7-P} \right)^{0.68} D^{1.73} H^{0.51} \Delta T^{0.5} F_p C K_c$
3.  $L_W = 1.09 \times 10^{-5} M P K_N K_C T_T$

where,  $L_T$  = total loss (Mg/yr)  
 $L_B$  = breathing loss (Mg/yr)

$L_W$  = working loss (Mg/yr)  
 $M$  = molecular weight; 154 lb/lb mole  
 $P$  = true vapor pressure; 1.4 at 60°F  
 $D$  = tank diameter; 26 ft.  
 $H$  = average vapor space height; assumed half of tank height; 16 ft.  
 $\Delta T$  = average ambient diurnal temperature change; 20°F  
 $F_P$  = point factor; 1.0 for clean white paint  
 $C$  = adjustment factor; approximately 1.0  
 $K_C$  = product factor; 1.0 for volatile organic compounds  
 $K_N$  = turnover factor; 0.73 for 50 turnovers  
 $T_t$  = tank throughput ( $10^3$  gal/yr); based on  $127 \times 10^3$  Mg/turnover  
 and 50 turnovers/yr;  $6350 \times 10^3$  Mg/yr.

Substituting the numbers into the equations yields:

$$L_B = (1.02 \times 10^{-5} (154) \left( \frac{1.4}{14.7 - 1.4} \right)^{0.68} (26)^{1.73} (16)^{0.51} (20)^{0.5} \\ (1.0)(1.0)(1.0)$$

$$L_B = 1.75 \text{ Mg/yr}$$

$$L_W = (1.09 \times 10^{-5}) (154) (1.4) (0.73) (1.0) (6350)$$

$$L_W = 10.89 \text{ Mg/yr}$$

$$L_T = 1.75 + 10.89 = 12.64 \text{ Mg/yr}$$

Therefore, working losses represent 86 percent of total losses.

Multiplying by the vapor balance control efficiency for working losses results in a control efficiency of 77 percent for total losses from carbon tetrachloride storage.

#### REFERENCES FOR APPENDIX A

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**APPENDIX B**  
**BASES FOR CAPITAL AND ANNUALIZED CONTROL COST ESTIMATES**

This Appendix provides technical data, control design calculations and other details related to control cost estimates in Chapters 3 through 6.

APPENDIX B-1  
PERCHLOROETHYLENE CO-PRODUCT PROCESS CONTROL

The following technical data were used to estimate the flow rate and refrigeration requirement for condensers which would control process vent emissions from perchloroethylene co-product plants, for cost estimates in Section 3.5.

- A. DuPONT/INGLESIDE (PLANT 7) PROCESS EMISSIONS  
(Ethylene feed, perchloroethylene co-product,  $\text{CCl}_4$  production capacity = 154,000 Mg/yr)

1. Carbon Tetrachloride Distillation

FLOW: 0.324 lb/hr

COMPOSITION (weight percent): 20%  $\text{CCl}_4$ , 50%  $\text{N}_2$ , 30%  $\text{COCl}_2$ .

TEMP: 30°C

<u><math>\text{CCl}_4</math> Emission Rates</u>	<u><math>\text{CCl}_4</math> Emission Factor</u>
0.0648 lb/hr = 568 lb/yr	
0.029 kg/hr = 258 kg/yr ÷ 154,000 Mg/yr = 0.0168 kg $\text{CCl}_4$ /Mg $\text{CCl}_4$	

2. Perchloroethylene Distillation

FLOW: 0.324 lb/hr

COMPOSITION (weight percent): 50%  $\text{CCl}_4$ , 50%  $\text{N}_2$

TEMP: 30°C

<u><math>\text{CCl}_4</math> Emission Rates</u>	<u><math>\text{CCl}_4</math> Emission Factor</u>
0.162 lb/hr = 1,419 lb/yr	
0.074 kg/hr = 645 kg/yr ÷ 154,000 Mg/yr = 0.0042 kg $\text{CCl}_4$ /Mg $\text{CCl}_4$	

### 3. Combined Distillation Vents

COMBINED RATES ABOVE:

<u>CCl<sub>4</sub> Emission Rates</u>	<u>CCl<sub>4</sub> Emission Factor</u>
0.029	0.00168
+ 0.074	+ 0.0042
0.103 kg/hr	0.0059 kg/Mg CCl <sub>4</sub>
258	
+ 645	
903 kg/yr	

FLOW RATE: 0.648 lb/hr; 0.294 kg/hr

TEMPERATURE: 30°C + 273.2 = 303.2°K

COMPOSITION

(weight percent):

	<u>Emission Rate</u>	<u>Molecular Wt.</u>	<u>Emission Rate</u>
35% CCl <sub>4</sub>	0.103 kg/hr	153.8 g/mole	0.67 mole/hr
50% N <sub>2</sub>	0.147 kg/hr	28 g/mole	5.25 moles/hr
15% COCl <sub>2</sub>	0.044 kg/hr	98.9 g/mole	0.48 mole/hr
	0.294 kg/hr		6.37 moles/hr

$$\text{VOLUME: } V (\text{ft}^3) = \frac{n RT}{P} = \frac{(6.37 \text{ g} \cdot \text{moles})(2.20 \text{ mm Hg} \cdot \text{ft}^3/\text{g} \cdot \text{mole} \cdot \text{°K})}{760 \text{ mm Hg}} (303 \text{ °K})$$

VOLUMETRIC FLOW RATE: 5.59 ft<sup>3</sup>/hr; 0.093 ft<sup>3</sup>/min

### 4. Basis of Data

DuPont calculated the original flow, composition and temperature data (1 and 2) based on system instrumentation and operating temperature, with some analytical data in (2). All original data from DuPont-designated Streams 2a and 3b, Reference 1.

### B. VULCAN/GEISMAR (PLANT 5) PROCESS EMISSIONS

(Ethylene dichloride and other mixed hydrocarbon feed; perchloroethylene co-product, CCl<sub>4</sub> production capacity = 41,000 Mg/yr)

### 1. Carbon Tetrachloride Distillation

Type of emission:	Intermittent
Flow during emission:	0.01 ft <sup>3</sup> /min
Normal emission:	None
Estimated intermittent emissions:	0.8 lb/day, 0.15 tons/yr CCl <sub>4</sub> (assumed to be uncontrolled rate)

This distillation vent is reported to be ducted directly to a crude  $\text{CCl}_4$  product tank, and then recycled through the process, under normal operating conditions.

2. Perchloroethylene Distillation

Type of emission:	Intermittent
Flow during emission:	0.003 ft <sup>3</sup> /min
Normal emission:	0.002 lb/hr, 0.01 tons/yr $\text{CCl}_4$

According to Vulcan, this vent had not had an emission for about 2 years when described in January 1977.

3. Combined Distillation Vents

The two vents above apparently would have a combined uncontrolled emission rate of about 0.035 lb/hr (0.016 kg/hr) and a maximum combined flow rate of 0.013 ft<sup>3</sup>/min. Annual combined uncontrolled emissions would be about 0.16 tons/yr (0.15 Mg/yr), for an emission factor of 0.004 kg/Mg. Note that although this emission factor was not used in earlier emission factor development due to the uncertain nature of these intermittent emissions, it correlates well with the 0.0059 kg/Mg derived from data for Plant 7 in A(3), above.

4. Basis of Data

Vulcan characterized all data presented above as their "rough estimates." All data are for Vulcan-designated emission sources #12 and #13, from Reference 2.

Tentative condenser design and costs were based on the following estimates of cooling and condensation required for the inlet composition for perchloroethylene co-product process vents shown in A(3), above. A condenser system reducing the outlet temperature to -20°C will reduce the carbon tetrachloride content to about 0.05 mole/hr. This reduction is based on an estimated emission reduction of 92 percent assumed to be associated with a 92 percent reduction of carbon tetrachloride's vapor pressure from 127 mm Hg at 30°C to 10 mm Hg at -20°C. (Information in B was only used to provide some perspective on the data in A, since designing for the intermittent flows at Plant 5 would require additional data. The relative size of the system designed below does appear to be capable of handling these flows, however.)

COOLING:

<u>Component</u>	<u>Content (in)</u>	<u>Heat capacity</u>	<u>Cooling requirement</u>
CCl <sub>4</sub>	0.67 mole/hr	19.9 cal/mole	13.3 cal/hr
COCl <sub>2</sub>	0.48 mole/hr	≈ 20 cal/mole	9.0 cal/hr
N <sub>2</sub>	5.25 mole/hr	7 cal/mole	36.7 cal/hr
			59.0 cal/hr

CONDENSATION:

Only carbon tetrachloride will condense out at -20°C:

$$0.67 \text{ mole/hr } \text{CCl}_4 \times 8,270 \text{ cal/mole} = 5,540 \text{ cal/hr} \text{ condensation requirement}$$

(heat of vaporization)

TOTAL REFRIGERATION REQUIREMENT: 59 + 5,540 ≈ 5,600 cal/hr  
≈ 22 BTU/hr

APPENDIX B-2  
METHANE CHLORINATION PROCESS CONTROL

The following technical data were used to estimate the flow rate and VOC emissions for the process vent at Plant 6, for Section 4.5.1.

DOW/FREEPORT (PLANT 6) PROCESS EMISSIONS

(methane chlorination, producing methyl chloride, methylene chloride, chloroform and carbon tetrachloride;  $\text{CCl}_4$  production capacity = 20,200 Mg/yr by this process)

Reaction Area Vents

FLOW: 325 lbs/hr; 148 kg/hr

COMPOSITION:

	Weight percent	Uncontrolled emission rate (kg/hr)	Molecular weight (g/mole)	Moles/hour
Oxygen	0.2	0.30	32	9.4
Nitrogen	21.3	31.5	28	1,125
Methane	47.7	70.6	18	3,922
Methyl chloride	30.0	44.4	50.5	879
Methylene chloride	0.76	1.12	85	13.2
Chloroform	0.05	0.07	119	0.6
Carbon tetrachloride	0.06	0.09	153.8	0.6
		148.08		5,955.2

TEMPERATURE: 30°C (estimated)

VOLUMETRIC FLOW RATE:

$$V(\text{ft}^3/\text{hr}) = \frac{n RT}{P} = \frac{(5,955.2 \text{ g} \cdot \text{moles}/\text{hr})(2.20 \text{ mm Hg} \cdot \text{ft}^3/\text{g} \cdot \text{mole} \cdot {}^\circ\text{K}}{760 \text{ mm Hg}}$$

$$V = 5,223 \text{ ft}^3/\text{hr}; 87 \text{ ft}^3/\text{min}$$

**BASIS OF DATA:**

Gas chromatograph and flow meter measurements. Original flow and composition data from Reference 3.

APPENDIX B-3  
CARBON DISULFIDE PROCESS CONTROLS: OPTIONS 1 AND 2

The following information relates to Section 5.5.

**A. CONTROL REQUIREMENTS**

To estimate Option 1 and Option 2 control costs for existing and retrofit refrigerated condensers at the Stauffer plant at Le Moyne, the reported current emissions and control efficiencies for the major process emission components were used to estimate uncontrolled emissions, emission reductions and the amount of refrigeration required, as shown below. The -62°C retrofit condenser was assumed to provide incremental control over the existing control of 95 percent, the efficiency for carbon tetrachloride estimated by vapor pressure reduction, for a net emission reduction of 99.8 percent. Preliminary calculations for a -40°C retrofit condenser are also shown for comparison purposes.

	Current (Option 1) emissions at full production after existing condenser <sup>b</sup>		Design removal efficiency of existing condenser (percent) <sup>6</sup>	Estimated uncontrolled emissions at full production	
	lb/hr	kg/hr		lb/hr	kg/hr
Carbon tetrachloride	120	54	95	2,400	1,090
Carbon disulfide	85	39	53	180	82
Sulfur chloride	46	21	95	920	418

The following physical constants were used to estimate cooling requirements for condensation, below (sensible heat loads were not considered since they are small relative to latent heat loads):

	<u>Molecular weight (g/mole)</u>	<u>Heat of vaporization (gm-cal/mole)</u>
Carbon tetrachloride	154	8,271
Carbon disulfide	76	6,787
Sulfur chloride	135	8,000 (assumed)

	Option 1: Existing condenser (-20°C)			
	Emission reduction kg/hr	Condensation required mol/hr	$10^6$ cal/hr	$10^3$ Btu/hr
Carbon tetrachloride	1,036	6,730	55.7	222
Carbon disulfide	43	570	3.9	16
Sulfur chloride	397	2,940	23.5	94
				332

	-40°C Condenser (retrofit to existing unit)			
	Estimated emissions (kg/hr)	Incremental reduction kg/hr	Condensation required mol/hr	$10^6$ cal/hr
Carbon tetrachloride	14.1	39.9	259	2.1
Carbon disulfide	10.1	28.9	380	2.6
Sulfur chloride	5.4	15.5	115	0.9
				3.7
				22.4

Option 2: -62°C condenser (retrofit to existing unit)					
<u>Estimated emissions (kg/hr)</u>	<u>Incremental reduction</u>		<u>Condensation required</u>		
	<u>kg/hr</u>	<u>mol/hr</u>	<u>10<sup>6</sup> cal/hr</u>	<u>10<sup>3</sup> Btu/hr</u>	
Carbon tetrachloride	2.7	51.3	333	2.8	10.9
Carbon disulfide	2.0	37.0	487	3.3	13.2
Sulfur chloride	1.1	19.9	148	1.2	4.7
					28.8

The refrigeration requirements for the existing and retrofit condensers are summarized as follows:

	<u>Refrigeration required</u>	
	<u>10<sup>3</sup> Btu/hr</u>	<u>Tons</u>
Existing condenser (-20°C)	332	28
Retrofit condenser (-40°C)	22	1.87
Retrofit condenser (-62°C)	29	2.40

## B. UTILITY COSTS FOR CARBON DISULFIDE PROCESS CONTROL

The electric utility rate used in 5.5.1 and 5.5.2 (\$0.080/KWH) is based on averages of national rates for four industrial size categories in January 1982 (\$0.075/KWH) inflated by 8 percent to July 1982. The 8 percent inflation for a half year was based on previous annual increases of 19 and 16 percent from 1980 through 1982.<sup>5</sup>

The cooling water cost was based on a 1980 EPA estimate of \$0.0733 per 1,000 gallons,<sup>6</sup> inflated by 49 percent to \$0.109 per 1,000 gallons. This 49 percent inflation factor is the result of compounding the rates from 1980 through July 1982, above, and was chosen because electricity for pumping is the principal cost for cooling water use.

Examples:

Cooling water cost for Option 1:

$$3 \text{ gpm/ton} \times 28 \text{ tons} \times (5.26 \times 10^5 \text{ min/yr}) \times \$0.109/10^3 \text{ g} = \$4,820/\text{yr}$$

Electricity for Option 1:

$$1.5 \text{ KW/ton} \times 28 \text{ tons} \times 8,760 \text{ hr/yr} \times \$0.082/\text{KWH} = \$29,000/\text{year}$$

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